

Aus der Poliklinik für Zahnerhaltung und Parodontologie  
der Ludwig-Maximilians-Universität München  
Direktor: Prof. Dr. R. Hickel

# **Einfluss von Wärme auf die mechanischen Eigenschaften von Zementen**

Dissertation  
zum Erwerb des Doktorgrades der Zahnheilkunde  
an der Medizinischen Fakultät der  
Ludwig-Maximilians-Universität zu München

vorgelegt von  
Ulrike Menne-Happ

aus München

2013

Mit Genehmigung der Medizinischen Fakultät  
der Universität München

Berichterstatter: PD Dr. Nicoleta Ilie

Mitberichterstatter: PD Dr. Andreas Fottner  
PD Dr. Michael Stimmelmayer  
Prof. Dr. Johannes Randzio

Dekan: Prof. Dr. med. Dr. h.c. M. Reiser, FACR, FRCR

Tag der mündlichen Prüfung: 19.11.2013

# Inhalt

<b>1. Einleitung</b>	<b>4</b>
1.1. Einführung	4
1.2. Material und Methode	5
1.3. Ergebnisse	9
1.4. Diskussion	10
1.5. Zusammenfassung	14
1.6. Conclusion	14
<b>2. Publikationen</b>	<b>15</b>
2.1. Effect of heat application on the mechanical behaviour of Glass Ionomer Cements	15
2.2. Effect of gloss and heat on the mechanical behaviour of a glass carbomer cement	33
<b>3. Literaturverzeichnis</b>	<b>54</b>

## **1. Einleitung**

### **1.1. Einführung**

Glasionomerzemente (GIZ) stellen in der Zahnheilkunde ein weit verbreitetes Material dar. Zum einen werden sie als Unterfüllung, Füllung und Fissurenversiegelung verwendet, aber auch zum Befestigen von Kronen, Brücken und kieferorthopädischen Bändern [1]. Als vorteilhaft werden bei GIZ die chemische Haftung an den Zahnhartsubstanzen, die hohe Fluoridabgabe sowie die fehlende Schrumpfung, verglichen mit Kompositen, gesehen [2, 3]. Aufgrund mangelnder Stabilität, der langen Abbindereaktion und mangelnder Toleranz gegenüber Feuchtigkeit und Austrocknung [1] werden stetig neue Zemente mit verbesserten Eigenschaften - laut Hersteller - entwickelt. Zur Verbesserung der Materialeigenschaften, zum Beispiel Biege- oder Abriebfestigkeit der herkömmlichen Zemente, wurden Metalle in die Glaspartikel eingeschmolzen (Ketac Silver) [4, 5]. Kunststoffmodifizierte (zum Beispiel Fuji II LC) und hoch visköse (beispielsweise Ketac Molar) GIZ erschienen auf dem Markt und vor kurzem wurde ein neuer Zement, Glass Carbomer Zement (GCP), entwickelt [4, 5]. Ebenso soll das Einschmelzen von Nanopartikeln (Nanohydroxyapatit und Nanofluorapatit) in die Matrix der Zemente [6] und die Anwendung von Ultraschall und Wärme [7] zu verbesserten mechanischen Eigenschaften führen. Wärme soll die langsame Abbindereaktion beschleunigen [8]. Dadurch wird die anfänglich kritische, feuchtigkeitsempfindliche Phase vor der Speichelkontamination verkürzt [9, 10] und die mechanischen Eigenschaften verbessert [7]. GCP ist ein Glass Carbomer Zement. Er besteht aus einem Fluorapatitglas, bei dem die Glaspartikel Nanogröße aufweisen [11]. GCP und seine klinische Anwendung ist mit konventionellen GIZ vergleichbar, mit der Besonderheit, dass der Hersteller Wärme während der Aushärtungsphase empfiehlt. Der zugehörige Lack ist ein silikonbasierter Lack, der den Zement vor Feuchtigkeit und Austrocknung während der Aushärtung schützen soll. Ältere Studien bewiesen gute und zum Teil überlegene mechanische Eigenschaften der Glass Carbomer Zemente verglichen mit GIZ [12, 13, 14, 15].

Das Ziel der Forschungsarbeiten zu dieser Dissertation war zu überprüfen, ob die Anwendung von Wärme einen Einfluss auf GIZ und GCP hat und ob der Lack die mechanischen Eigenschaften von GCP beeinflusst. Als Erstes wurden die mikromechanischen Parameter wie die Vickershärte, das

mikroskopische Elastizitätsmodul (Emirko) und das Kriechverhalten von fünf konventionellen, hoch viskösen GIZ unter verschiedenen Temperaturbedingungen und Lagerzeiten verglichen. Im zweiten Teil wurden makromechanische Parameter (Biegefestigkeit und Elastizitätsmodul im Drei-Punkt-Biegeversuch) und mikromechanische Parameter (Vickershärte, Emikro und Kriechverhalten) von GCP in Abhängigkeit von der Verwendung eines Lacks und unter unterschiedlichen Temperaturbedingungen gemessen und die Werte mit kunststoffmodifizierten GIZ verglichen.

Die Frage nach dem Einfluss der Temperatur auf die mechanischen Eigenschaften von Zementen verbindet die Thematiken zweier Publikationen: „*Effect of heat application on the mechanical behaviour of Glass Ionomer Cements*“, von Ulrike Menne-Happ und Nicoleta Ilie, veröffentlicht im Clinical Oral Investigations (angenommen am 22. Mai 2013), und „*Effect of gloss and heat on the mechanical behaviour of a glass carbomer cement*“ von Ulrike Menne-Happ und Nicoleta Ilie, veröffentlicht im Journal of Dentistry im März 2013, Ausgabe 41(3):223-230. Bei beiden Veröffentlichungen lag der Fokus auf der Untersuchung mechanischer Parameter abhängig von der Temperatur. In der ersten Studie wurde der Fokus besonders auf die Langzeitwirkung gelegt, wohingegen in der zweiten Studie nicht nur der Einfluss der Temperatur, sondern auch der eines Lacks auf den neu entwickelten Zement GCP untersucht wurde.

## **1.2. Material und Methode**

Für die erste Versuchsreihe wurden fünf verschiedene, hoch visköse GIZ verwendet: ChemFil Rock, Riva Self Cure, Fuji IX GP Fast, Fuji IX GP Extra/Equia und Ketac Molar Aplicap. Die beiden kunststoffmodifizierten GIZ, Fuji II LC und Photac Fil Quick Aplicap, sowie das kürzlich auf dem Markt gekommene GCP waren die Materialien der zweiten Versuchsreihe (siehe Tabelle Seite 6). Alle Zemente wurden in Kapselform und in der Farbe A3 verwendet.

**Tabelle:** Material, Hersteller, Lotnummer und Angaben der Inhaltsstoffe der Zemente

<b>Material</b>	<b>Hersteller</b>	<b>Lotnummer</b>	<b>Inhaltsstoffe</b>
ChemFil Rock	Dentsply, Konstanz	1105000885	Kalzium-Aluminium-Zink-Fluoro-Phosphor-Silikatglas, Polycarboxysäure, Eisenoxid Pigmente, Titaniumdioxid Pigmente, Tartarsäure, Wasser
Riva Self Cure	SDI Limited, Victoria, Australien	B0912111	Fluoro-Aluminosilikatglas, Polyacrylsäure, Tartarsäure
Fuji IX GP Fast	GC Europe N.V., Leuven, Belgien	1005211	Alumino-Fluorosilikatglas, Polyacrylsäure, mehrbasische Carboxysäure, destilliertes Wasser
Fuji IX GP Extra/Equia	GC Europe N.V., Leuven, Belgien	1005281	Aluminosilikatglas, Polyacrylsäure, destilliertes Wasser
Ketac Molar Aplicap	3M ESPE, Seefeld	70201103911	Kalzium-Aluminium-Lanthanum-Fluorosilikatglas, Copolymer der Acrylsäure und Maleinsäure, Tartarsäure
Fuji II LC capsule	GC Europe N.V., Leuven, Belgien	1109107	Alumino-Fluorosilikatglas, Polyacrylsäure, 2-Hydroxyethylmethacrylat, 2,2,4-Trimethyl Hexamethylene Dicarbonat, Triethylen Glycol Dimethacrylat
Photac Fil Quick Aplicap	3M ESPE, Seefeld	454040	Natrium-Kalzium-Aluminium-Lanthanum-Fluorosilikatglas, 2-Hydroxyethylmethacrylat, difunktionelle Monomere, Aktivator (Amin), Copolymer der Acrylsäure und Maleinsäure, Camphorquinone Stabilisator
GCP Glass fill & gloss GCP 1: ohne Lack, ohne Wärme GCP 2: ohne Lack, mit Wärme GCP 3: mit Lack, ohne Wärme GCP 4: mit Lack, mit Wärme	GCP Dental, Vianen, Holland	7103067 1104070	Fill: Fluoro-Aluminosilikatglas, Apatit, Polysäuren Gloss: modifizierte Polysiloxane

Die Proben wurden in einer rostfreien Stahlmatrize produziert. Hierbei wurde der jeweilige Zement in eine 6 x 2 x 2 mm (Versuchsreihe 1) beziehungsweise 16 x 2 x 2 mm (Versuchsreihe 2) messende Form appliziert und dann zwischen zwei planparallelen Glasplatten und durch einen durchsichtigen Frasacostreifen ausgeformt. Um der klinischen Situation möglichst nahe zu kommen, befand sich die Matrize 20 Minuten lang auf einem 37°C warmen Ofen.

Die Stäbchen der ersten Versuchsreihe wurden nach drei verschiedenen Methoden hergestellt: 1) keine zusätzliche Wärme, 2) 20 Sekunden Wärme und 3) 60 Sekunden Wärme. Die Wärmebehandlung erfolgte eine Minute nach dem Anrühren mittels einer LED-Lampe (Bluephase, Ivoclar Vivadent, Intensität:  $1435 \text{ mW/cm}^2$ ) auf der Oberfläche der Proben. Nach der Herstellung wurden die Proben vorsichtig aus der Matrize entfernt und in drei Gruppen aufgeteilt. Der erste Teil wurde eine Woche, der zweite einen Monat und der dritte drei Monate in destilliertem Wasser bei  $37^\circ\text{C}$  gelagert. Das destillierte Wasser wurde zweimal wöchentlich ausgetauscht. Die mechanischen Eigenschaften der fünf GIZ wurden bei drei verschiedenen Temperaturbedingungen (keine Wärme, 20 Sek. und 60 Sek. Wärme) und drei verschiedenen Lagerungszeiten (eine Woche, ein Monat, drei Monate) gemessen. Folglich entstanden 45 Gruppen und insgesamt 450 Proben ( $n=10$ ).

Die Herstellung der Proben für die zweite Versuchsreihe erfolgte ähnlich. Die kunststoffmodifizierten GIZ wurden von beiden Seiten mit der oben genannten Lampe 20 Sekunden lang polymerisiert. Der Lichtleiter der Lampe wurde dreimal pro Seite auf die Probe aufgesetzt, wobei sich dabei die Durchmesser der Lichtkreise nicht um mehr als einen Millimeter überlappen durften, um eine mehrfache Polymerisation zu verhindern. Bei den GCP-Proben wurden vier verschiedene Herstellungsvarianten verwendet: 1) keine Wärme und kein Lack (GCP 1), 2) kein Lack, aber Wärme (GCP 2), 3) Lack, aber keine Wärme (GCP 3), 4) Lack und Wärme (GCP 4) (siehe Tabelle Seite 6). Die Wärme wurde mit der LED-Lampe für 20 Sekunden wie bei den kunststoffmodifizierten GIZ beschrieben appliziert. Die Proben wurden nach 20 Minuten vorsichtig aus der Matrize entfernt und eine Woche in destilliertem Wasser bei  $37^\circ\text{C}$  gelagert. Pro Gruppe wurden 20 Stäbchen hergestellt, was eine Gesamtzahl von 120 Proben ergab ( $n=20$ ). Nach der Lagerung erfolgte die Bearbeitung der Proben mit Schleifpapier aus Siliziumcarbid der Körnung 1200 (LECO, St. Joseph, MI, USA), um eventuelle Kanten zu brechen und Überschüsse zu entfernen.

Bei den Proben der ersten Versuchsreihe wurden die mikromechanischen Eigenschaften im Universalhärteversuch (Fisherscope H100C, Fischer, Sindelfingen) bestimmt. Bei den Proben der zweiten Versuchsreihe wurden zuerst die makromechanischen Eigenschaften im Biegeversuch und anschließend die mikromechanischen Eigenschaften im Universalhärteversuch ermittelt.

Zur Untersuchung der makromechanischen Parameter (Biegefestigkeit und Elastizitätsmodul) wurden die stäbchenförmigen Proben vermessen und anschließend in einer Universalprüfmaschine (Zwick/Roell Z 2.5, Ulm und test Xpert II software) in einem Drei-Punkt-Biegeversuch bis zum Bruch mit einer konstanten Geschwindigkeit von 0,5 mm/min belastet (Versuchsreihe 2). Während der gesamten Prüfzeit waren die Proben komplett mit destilliertem Wasser bei Raumtemperatur bedeckt. Gemessen wurde die Prüfkraft in Newton in Abhängigkeit von der Dehnung der Zemente bis zum Bruch der Probe.

Die Biegefestigkeit  $\sigma$  wurde mit folgender Gleichung berechnet:

$$\sigma = \frac{3Fl}{2bh^2}$$

Das Elastizitätsmodul  $E_{flexural}$  wurde mit Hilfe dieser Gleichung berechnet:

$$E_{flexural} = \frac{Fl^3}{4bh^3y}$$

F ist die maximale Kraft [N], l der Abstand zwischen den Widerlagern [mm], b die Breite der Proben [mm], h die Höhe der Proben [mm] und y die Durchbiegung bei Belastung [mm].

Zur Untersuchung der mikromechanischen Eigenschaften wurden jeweils sechs Stäbchen (Versuchsreihe 1) und sechs beim Biegeversuch entstandene Bruchhälften (Versuchsreihe 2) nebeneinander auf einen Objektträger aufgeklebt. Diese wurden mit Hilfe von Schleifpapier der Körnung 2500/4000 (Hermes, Virginia Beach, VA, USA) aus Siliziumcarbid bearbeitet, auf dieselbe Höhe geschliffen und poliert. Die mikromechanischen Eigenschaften (Vickershärte, Emikro und Kriechverhalten) wurden in einem Universalhärteversuch getestet. Bei diesem Messverfahren wird ein pyramidenförmiger Diamant (Vickerspyramide) mit bekannter Geometrie auf die polierten Proben aufgesetzt und mit kontinuierlich gesteigerter Prüfkraft (von 0 - 500 mN) in diese vertikal hineingedrückt. Nach erreichter maximaler Prüfkraft von 500 mN wird diese fünf Sekunden konstant beibehalten, bevor die Prüfkraft wieder kontinuierlich bis auf null reduziert wird. Die wirkende Prüfkraft und die Eindringtiefe der Vickerspyramide werden während des gesamten Prüfvorganges fortlaufend gemessen. Das Resultat



der Messung ist ein Prüfkraft-Eindringtiefe-Verlauf für die Be- und Entlastung, aus dem sich wichtige Parameter ableiten lassen. Die Vickershärte wird von der Herstellersoftware durch Umrechnung aus der Universalhärte bestimmt. Das Elastizitätsmodul lässt sich aus der Steigung der Tangente an der Entlastungskurve bei maximaler Kraft von 500 mN ableiten. Aus der fünf Sekunden konstant gehaltenen Prüfkraft bei 500 mN und den Messwerten der veränderten Eindringtiefe über die Haltezeit wird das Kriechverhalten berechnet.

Die Oberfläche der Proben wurde im Lichtmikroskop der Universalhärteprüfmaschine bei der Messung der mikromechanischen Eigenschaften sowie anschließend in einem Elektronenmikroskop (SEM, Zeiss Supra 55 VP, Carl Zeiss AG, Oberkochen) untersucht. Die Größe, Anzahl und Verteilung der Blasen und Glasfüller innerhalb der GCP-Gruppen und unter den Zementen wurden verglichen.

### **1.3. Ergebnisse**

Die Untersuchungen des Universalhärtegerätes der ersten Prüfreihe ergaben eine mittlere Vickershärte von  $115,6 \text{ N/mm}^2$  (Equia, 3 Monate Lagerung) bis  $58,7 \text{ N/mm}^2$  (ChemFil Rock, eine Woche Lagerung). Das größte Emikro wurde bei Ketac Molar Aplicap (28,5 GPa, ein Monat Lagerung) gemessen, während ChemFil Rock (17,4 GPa, eine Woche Lagerung) den kleinsten Wert aufwies. Ebenso erreichte ChemFil Rock den höchsten und somit schlechtesten Mittelwert im Kriechverhalten (4,9 %, eine Woche Lagerung). Das geringste, somit beste Kriechverhalten wurde bei Riva Self Cure gemessen (3,5 %, drei Monate Lagerung). Statistische Untersuchungen ergaben, dass die Art des verwendeten Zements den größten Einfluss auf die mikromechanischen Eigenschaften hat, gefolgt von der Lagerzeit (vor allem bei ChemFil Rock, Equia und Ketac Molar Aplicap). Die Wärmezufuhr zeigte keinen Einfluss auf die mikromechanischen Eigenschaften der Zemente mit Ausnahme von Ketac Molar Aplicap (Vickershärte und Elastizitätsmodul) und Riva Self Cure (Elastizitätsmodul). Jedoch wurde bei diesen beiden Zementen lediglich ein sehr geringer Einfluss gemessen. Bei Betrachtung der Proben im Lichtmikroskop der Universalhärteprüfmaschine sowie im Elektronenmikroskop fielen kleineren Blasen bei Ketac Molar Aplicap im Gegensatz zu großen Blasen bei ChemFil Rock und Riva Self Cure auf. Die größten Füller wurden bei Riva Self Cure, Equia und

Fuji IX GP Fast entdeckt, wohingegen ChemFil Rock und Ketac Molar Aplicap viele kleine Füller in der Matrix enthielten.

Die zweite Versuchsreihe zeigte eine mittlere Biegefestigkeit von 61,8 MPa und 58,0 MPa bei den kunststoffmodifizierten GIZ, Fuji II LC und Photac Fil. Die GCP-Gruppen erreichten mit 9,5 - 10,1 MPa lediglich ein Sechstel der gemessenen Werte der kunststoffmodifizierten GIZ. Bei Betrachtung des Elastizitätsmoduls erzielten GCP und Fuji II LC die höchsten, somit besten Mittelwerte (3,8 - 4,8 GPa), während für Photac Fil der geringste Wert gemessen wurde (2,6 GPa). Die Untersuchungen im Universalhärtegerät ergaben eine mittlere Vickershärte von 57,9 - 68,5 N/mm<sup>2</sup> (Fuji II LC und GCP) und 45,5 - 48,6 N/mm<sup>2</sup> (Photac Fil). Ebenso wurden das größte Emikro für Fuji II LC und GCP (14,9 - 13,4 GPa) gemessen (Photac Fil: 13,2 - 12,8 GPa). Das Kriechverhalten erstreckte sich von 3,6 - 4,2 % (GCP) bis 5,0 - 5,6 % (kunststoffmodifizierte GIZ). Zwischen den einzelnen GCP-Gruppen - abhängig von der Lack und Wärmebehandlung - ließen sich keine Unterschiede erkennen. Statistische Untersuchungen bestätigten, dass auch hier der verwendete Zement den größten Einfluss auf die mechanischen Eigenschaften hat. Bei der Untersuchung der mikromechanischen Parameter zwischen Ober- und Unterseite der Proben der zweiten Versuchsreihe waren keine Unterschiede erkennbar. Im Lichtmikroskop der Universalhärteprüfmaschine und im Elektronenmikroskop zeigten sich mehr Blasen und Risse auf der Stäbchenoberfläche bei GCP als bei den kunststoffmodifizierten GIZ. Die kunststoffmodifizierten GIZ wiesen, verglichen mit GCP, eine ähnliche Matrix mit deutlich größeren Füllern auf. Fuji II LC und GCP beinhalteten mehr Füller als Photac Fil.

#### **1.4. Diskussion**

Die beiden Versuchsreihen untersuchten den Einfluss von Wärme auf die mechanischen Eigenschaften von Zementen. Zusätzlich wurde in der ersten Versuchsreihe der besondere Fokus auf den Langzeiteffekt gelegt. In der zweiten Versuchsreihe wurde neben dem Einfluss von Wärme auch der eines Lacks auf einem neu auf dem Markt erhältlichen Glas Carbomber Zements untersucht. Außerdem wurden die mechanischen Eigenschaften mit bekannten kunststoffmodifizierten GIZ verglichen.

Die Wärmebehandlung zeigte weder auf die konventionell, hoch viskösen GIZ (ChemFil Rock, Fuji IX GP Fast und Equia) noch auf GCP einen Einfluss. Die mechanischen Eigenschaften waren hauptsächlich von der Art des verwendeten Zements abhängig.

Woolford nahm an, dass die Verwendung von Wärme die Abbindereaktion der Zemente beschleunigt und so eher eine größere Oberflächenhärte erreicht wird [10]. Die Zemente enthalten unterschiedliche Füller und Säuren (siehe Tabelle Seite 6). Die Wärmezufuhr soll zu einer schnelleren Aktivierung der Säuren führen, sodass diese eher und frühzeitig mit den Glasfüllern reagieren [10]. Das wiederum führt zu einer schnelleren Bildung der Kalziumpolyacrylatmatrix, dem ersten Produkt der Abbindereaktion [10]. Die Wärmebehandlung der Zemente verbesserte deren mechanische Eigenschaften in der frühen Abbindephase, in der diese sehr empfindlich gegenüber Feuchtigkeit sind. Frühere Versuche zeigten, dass eine Zufuhr von Energie wie das Vorheizen der Zementkapseln ( $40 \pm 1^\circ\text{C}$  für 90 Sek. vor der Aktivierung), die Verwendung einer Halogenlampe (Optilux 501, Kerr UK Ltd., Peterborough, Großbritannien; bei  $1012 \pm 20 \text{ mW cm}^{-2}$  für 40 Sek.) oder Ultraschall (P-tip Ultraschallscaler betrieben durch einen Mini-Piezon US Generator, EMS, Nyon, Schweiz; bei 30 kHz, Stufe 1 für 40 Sek.) 30 Minuten nach dem Anmischen zu einer höheren Oberflächenhärte führte im Vergleich zu GIZ ohne externer Energiezufuhr [16]. Ebenso zeigte die Verwendung von Infrarotlicht (Phillips Electrical, Holland; bei  $80^\circ\text{C}$  für 60 Sek.) oder Halogenlicht (Litema GSD, Baden-Baden; für 20, 40 und 60 Sek.) bei Chemfil II (DeTrey Division, Dentsply, Weybridge, Surrey, Großbritannien) eine deutlich erhöhte Härte nach 24 Stunden im Vergleich zu einem nicht wärmebehandelten Zement [10]. Wärme beschleunigt die Abbindereaktion [8, 10], verändert jedoch langfristig die mechanischen Eigenschaften der Zemente nicht.

Ein Grund für die unterschiedlichen Messergebnisse bei demselben Zement in Abhängigkeit von der Lagerzeit ist die unvollständige Abbindereaktion und somit schwächere mechanische Eigenschaften nach einer Woche im Vergleich zu drei Monaten. Frühere Studien belegten, dass die Härte von GIZ (zum Beispiel Fuji IX GP) nach einem Tag signifikant geringer war, als nach einer Woche oder einem Monat [17]. Der Aushärtungsprozess erfolgt nach der Bildung der Kalziumpolyacrylatmatrix durch die Bildung von Aluminiumsalzbrücken und Bindung von Wasser [18]. Die Lagerung von Zementen

verstärkt die Matrix und führt zu verbesserten mechanischen Eigenschaften aufgrund der langsamen Abbindereaktion.

Die Benutzung eines Lacks bei GCP zeigte keinen Einfluss auf die nach einer Woche gemessenen mechanischen Parameter. Wegen ihrer Feuchtigkeitsempfindlichkeit sind Zemente sehr techniksensibel [19]. Die Oberfläche von Zementen sollte mit einem Lack vor Feuchtigkeit und Austrocknung geschützt werden [19]. Die Lackapplikation bei konventionellen GIZ (Riva Self Cure, Chemfil Rock, Fuji IX GP Fast, Equia) führte zu einer signifikant höheren Biegefestigkeit [20], wohingegen Lack bei GCP keinen Einfluss auf die mechanischen Eigenschaften zeigte. Ein Grund dafür kann die unterschiedliche chemische Zusammensetzung und somit unterschiedliche Feuchtigkeitsempfindlichkeit sein. Der GCP-Lack ist frei von Monomeren und besteht aus modifizierten Polysiloxanen (siehe Tabelle Seite 6), wohingegen Lacke zum Schutz von GIZ üblicherweise aus Monomeren bestehen, die polymerisiert werden können.

Die Untersuchung der makromechanischen Eigenschaften nach einer Woche zeigte, dass GCP den getesteten kunststoffmodifizierten GIZ unterlegen ist. Ebenso waren die konventionellen GIZ (Fuji IX, GC, Leuven, Belgien und Ionofil Molar, Cuxhaven) den kunststoffmodifizierten GIZ (Fuji II LC Improved, Photac Fil) nach 24 Stunden unterlegen [21]. Beim Vergleich von GCP mit konventionellen GIZ (Riva Self Cure, Chemfil Rock, Fuji IX GP Fast und Equia) bei denselben Versuchsbedingungen wurde eine größere Biegefestigkeit für die konventionellen GIZ nach einer Woche gemessen (14,3 - 39,4 MPa) [20]. Jedoch zeigten andere Studien nach 24 Stunden eine größere Biegefestigkeit für GCP als für den konventionellen GIZ Fuji IX GP Fast [15]. Das kann sich durch die Nanopartikel in der GCP Matrix erklären lassen, die zu einer schnelleren Abbindereaktion aufgrund der vergrößerten Oberfläche führen und somit überlegenen mechanischen Eigenschaften in der frühen Abbindephase (siehe auch Seite 13, Zeile 5-8).

Anders als die makromechanischen Eigenschaften waren die gemessenen mikromechanischen Werte von GCP den kunststoffmodifizierten GIZ überlegen. Im Vergleich zu konventionellen GIZ (Riva Self Cure, Chemfil Rock, Fuji IX GP Fast und Equia; VH: 66,8 - 125,9 N/mm<sup>2</sup>; E: 17,1 - 25,7 GPa) zeigte GCP schlechtere mikromechanische Eigenschaften bei denselben Versuchsbedingungen [20]. Die relative Eindringtiefe bei konstant gehaltener Prüfkraft von 500 mN für fünf Sekunden ist ein

Messwert, der das Kriechverhalten angibt und ein weiterer wichtiger Parameter, der die mechanischen Eigenschaften eines Materials bestimmt. Mit einer relativen Eindringtiefe von 3,6 - 4,2 % bietet GCP eine größere Stabilität unter Belastung als die kunststoffmodifizierten GIZ (5,0 - 5,6 %).

Beim Vergleich der Mikrostruktur, der Zusammensetzung und der mechanischen Eigenschaften können gewisse Beziehungen erkannt werden. Die Abbindereaktion und die mechanischen Eigenschaften der Zemente werden unter anderem von der Füllergröße und deren Anzahl in der Matrix beeinflusst. Kleine Füller vergrößern die Oberfläche und bieten deshalb dem Säureangriff eine größere Fläche [22]. Dadurch verringert sich die Abbindezeit [22]. Chemfil Rock und Ketac Molar Aplicap beinhalten kleine Glasfüller, jedoch unterscheiden sich die mechanischen Eigenschaften dieser beiden Zemente deutlich. Grund dafür können eine unterschiedliche Blasengröße und die chemische Zusammensetzung sein (siehe Tabelle Seite 6). Das Kalzium-Aluminium-Zink-Fluoro-Phosphor-Silikatglas von ChemFil Rock ist schwächer als das Kalzium-Aluminium-Lanthanum-Fluorosilikatglas von Ketac Molar Aplicap. Nach Angaben des Herstellers soll das Zink beinhaltende Glas von ChemFil Rock die Abbindereaktion beschleunigen und zu besseren mechanischen Eigenschaften führen. Frühere Studien belegen überlegene makromechanische Werte (Biegefestigkeit) von ChemFil Rock verglichen mit Riva Self Cure, Fuji IX GP Fast und Equia nach einer Woche und einem Monat [20]. Jedoch zeigte ChemFil Rock die niedrigste Vickershärte und Elastizitätsmodul [20]. Folglich ist bei Betrachtung der mikromechanischen Eigenschaften das Aluminosilikatglas der getesteten Zemente dem Zinkglas von ChemFil Rock überlegen.

Die gemessenen Werte ergeben eine signifikant höhere Biegefestigkeit für die kunststoffmodifizierten GIZ, wohingegen GCP eine größere Vickershärte und kleinere und somit bessere Werte im Kriechverhalten zeigt. Die größeren Glaspartikel, weniger Blasen und Risse in der Matrix der kunststoffmodifizierten GIZ ergeben eine größere Biegefestigkeit. Die kleineren Glaspartikel in der GCP-Matrix führen zu einer größeren Vickershärte und kleinerem Kriechverhalten. Die Nanopartikel vergrößern die reaktive Oberfläche von GCP und führen zu einer größeren Härte [23]. Fuji II LC und GCP erreichten signifikant höhere Elastizitätsmoduli als Photac Fil aufgrund einer größeren Anzahl an Glasfüllern in der Matrix. Die chemische Zusammensetzung und unterschiedlichen Polymere sind weitere Gründe für die unterschiedlichen mechanischen Eigenschaften der kunststoffmodifizierten

GIZ und GCP. Die Zemente bestehen aus Silikatglas, wobei die kunststoffmodifizierten GIZ auch Monomere (siehe Tabelle Seite 6) beinhalten, die polymerisiert werden können. Auch das dualhärtenden System (selbsthärtend und lighthärtend) der kunststoffmodifizierten GIZ trägt zu einer höheren Biegefestigkeit bei [24].

### **1.5. Zusammenfassung**

Die Wärmebehandlung zeigte weder bei konventionell, hoch viskösen GIZ (ChemFil Rock, Fuji IX GP Fast und Equia), noch bei Glass Carbomer Zement eine Veränderung der mechanischen Eigenschaften. Diese waren hauptsächlich von der Art des verwendeten Zements abhängig. Die Lagerung der GIZ zeigte einen geringen Einfluss auf die mechanischen Parameter. Für ChemFil Rock und Equia wurde bei einem Monat Lagerzeit der größte Anstieg der gemessenen mechanischen Werte beobachtet. In der zweiten Versuchsreihe überragten die kunststoffmodifizierten GIZ bei den makromechanischen Versuchen GCP, während GCP bezüglich der mikromechanischen Parameter dominierte. Ebenso wie Wärme beeinflusste der Lack die mechanischen Eigenschaften von GCP nicht.

### **1.6. Conclusion**

Statistical analysis revealed that heat application showed neither an effect on the conventional glass ionomer cements (ChemFil Rock, Fuji IX GP Fast and Equia) nor on GCP. Also, no effect of gloss application on the mechanical properties of GCP was measured. The impact of storage duration was low. Vickers Hardness, modulus of elasticity and creep resistance increased most for ChemFil Rock and Equia up to one month storage. In the second test, macroscopically, the resin-modified glass ionomer cements performed significantly better than GCP. Conversely, in the microhardness test, GCP was superior to the resin-modified glass ionomer cements. The mechanical properties were basically influenced by the type of cement.

## 2. Publikationen

Zwei Publikationen wurden bei dentalen Fachmagazinen eingereicht und akzeptiert: im Clinical Oral Investigations und im Journal of Dentistry. Beim Clinical Oral Investigations steht die Drucklegung noch aus („*Effect of heat application on the mechanical behaviour of Glass Ionomer Cements*“ von Ulrike Menne-Happ und Nicoleta Ilie, angenommen von Clinical Oral Investigations am 22. Mai 2013). Im Journal of Dentistry wurde die Publikation bereits veröffentlicht („*Effect of gloss and heat on the mechanical behaviour of a glass carbomer cement*“ von Ulrike Menne-Happ und Nicoleta Ilie, Journal of Dentistry, Volume 41, Issue 3, März 2013, Seite 223-230).

### 2.1. Effect of heat application on the mechanical behaviour of Glass Ionomer Cements

#### Abstract

*Objectives:* The aim of this study was to examine the long-term effect of heat on the mechanical behaviour of conventional highly viscous glass ionomer cements. Besides, the effect of storage time was evaluated.

*Materials and methods:* Five cements (ChemFil Rock, Riva Self Cure, Fuji IX GP Fast, Equia and Ketac Molar Aplicap) were evaluated using three different preparation methods: no heat application, application of heat by means of a LED curing unit for 20 and 60 seconds. 450 bar-shaped specimens were produced, maintained in distilled water at 37°C and tested after one week, one month and three months (n = 10). The Vickers Hardness, indentation modulus and creep were measured. In addition, the amount and size of the glass fillers and voids were examined using a light and a scanning electron microscope.

*Results:* Fuji IX GP Fast showed the highest Vickers Hardness, Ketac Molar Aplicap the highest indentation modulus and the best value of creep was measured for Riva Self Cure. Vickers Hardness, modulus of elasticity and creep resistance increased most for ChemFil Rock and Equia up to one month storage.

*Conclusions:* Heat application showed no effect on the mechanical behaviour of ChemFil Rock, Fuji IX GP Fast and Equia at all aging time. The impact of storage duration was low.

*Clinical Relevance:* Considering the measured mechanical properties, there is no need of using heat when restoring teeth with glass ionomer cements.

## **Introduction**

In an attempt to improve the mechanical characteristics of glass ionomer cements (GICs) several studies suggest applying heat during the setting reaction of the cements [1, 2]. GICs are acknowledged for their chemical adhesion to enamel and dentine [3], continuing fluoride release [4] and tooth colour [5]. The major drawbacks of GICs have been the lack of physical strength, moisture sensitivity, inherent opacity [6] and the slow curing reaction [7]. So, for use in large stress-bearing posterior cavities as permanent restorations, conventional GICs were previously not considered material of choice [8-10]. However highly viscous GICs used for single-surface atraumatic restorative treatment (ART) restorations show a potential for restoring and saving posterior permanent teeth [11] and are frequently recommended in primary teeth [12].

The setting reaction of GICs is divided into two phases: an initial set with the formation of mainly calcium polyacrylate which occurs within the first 10 minutes after mixing and a subsequent long-term hardening process with the formation of aluminium polyacrylate [7, 13]. During the first reaction, GICs are very susceptible to water or saliva contamination and in the second phase to dehydration [7, 13, 14]. The initial moisture-sensitivity results in a susceptibility to fracturing and initial wear [7]. In the initial stages of the setting reaction, a high proportion of loosely bound water is present in the cements [15]. If this is lost by desiccation or if water or saliva contacts the cement, the cement forming ions will be washed out resulting in a decrease in physical strength and loss of translucency [15]. Ongoing developments have led to improved GICs. Manufacturers added silver (Ketac Silver, 3M ESPE, Seefeld, Germany) [16], resin-modified GICs were introduced [3], the viscosity was increased by reducing filler size (Ketac Molar, 3M ESPE, Seefeld, Germany) [16] and heat application was suggested [1, 2]. Heat application is supposed to accelerate the slow setting reaction [17] and thus, skipping over the initial sensitive period before exposure to saliva occurs [1, 2]. The heat energy can be supplied by the use of a high energy LED, halogen lamp or ultrasonic excitation [18, 19, 20]. The compressive strength of GICs (e.g. Fuji IX GP Fast, GC Europe N.V., Leuven, Belgium) was affected by heat application [7]. At early setting stage, a significant increase in the compressive strength was



measured compared to the standard setting reaction of the material (for ultrasonic excitation 65% increase in strength after 15 minutes and 21% after 1 day and for heat application 130% after 15 minutes and 24% after 1 day) [7]. An obvious relationship between temperature of the GIC samples (70°C) and their compressive strength was observed [7]. In addition, the compressive strength of GICs was shown to increase during 28 days [7]. It has been previously reported that the hardness of GICs gradually increased over one month to a value significantly greater than the recorded value at 24 h [21]. Considering the early surface hardness (0.5 hours - 1 week) the use of an external energy source such as preheating capsules, application of halogen or infrared light or ultrasonic energy resulted in a significantly improved upper surface hardness of GICs [2, 22].

The objective of this study was to assess the long-term effect of heat on the mechanical behaviour of five conventional highly viscous GICs by determining several mechanical properties at microscopic scale: Vickers Hardness, indentation modulus and creep.

The following null hypotheses were tested: i) there would be no differences in the measured properties of the GICs when heat is applied; ii) no differences would exist at different storage times; iii) the five GICs would perform similarly in all mechanical properties.

## Materials and methods

The five GICs used are listed in Table 1 (ChemFil Rock, Riva Self Cure, Fuji IX GP Fast, Fuji IX GP Extra/Equia and Ketac Molar Aplicap), together with the manufacturer, batch number and chemical composition according to the material safety data sheet. All GICs were supplied in encapsulated form and in shade A3.

**Table 1** Material, manufacturer, batch number and chemical composition of the GICs

Material	Manufacturer	Batch no.	Chemical composition
ChemFil Rock	Dentsply, Konstanz, Germany	1105000885	calcium-aluminium-zinc-fluoro-phosphor-silicate glass, polycarboxylic acid, iron oxide pigments, titanium dioxide pigments, tartaric acid, water
Riva Self Cure	SDI Limited, Victoria, Australia	B0912111	fluoro-aluminosilicate glass, polyacrylic acid, tartaric acid
Fuji IX GP Fast	GC Europe N.V., Leuven, Belgium	1005211	alumino-fluorosilicate glass, polyacrylic acid, polybasic carboxylic acid, distilled water

Material	Manufacturer	Batch no.	Chemical composition
Fuji IX GP Extra/Equia	GC Europe N.V., Leuven, Belgium	1005281	aluminosilicate glass, polyacrylic acid, distilled water
Ketac Molar Aplicap	3M ESPE, Seefeld, Germany	70201103911	calcium-aluminium-lanthanum-fluorosilicate glass, copolymer of acrylic acid and maleic acid, tartaric acid

*Vickers Hardness, indentation modulus and creep*

450 bar-shaped specimens, measuring 6 mm x 2 mm x 2 mm, were produced out of the five GICs by using a stainless steel mould. In order to simulate clinical conditions the mould was placed on a heater (Präzitherm PZ 34, Bachofer, Reutlingen, Germany) at 37°C. The GICs were used according to the manufacturers' instructions and mixed for 10 seconds with a RotoMix (3M ESPE, Seefeld, Germany). After injecting uncured cement into the mould, the samples were covered with transparent matrix strips (Matrix-Strips, Orbis, Münster, Germany) and shaped between two parallel glass plates. The matrix strips are supposed to simulate the coating and protect the GICs from loss or gain of moisture. The samples were prepared according to three different conditions: 1) no additional heat application, 2) heat application for 20 seconds and 3) heat application for 60 seconds. The heat was applied on the top surface by using a light-emitting diode (LED) curing unit (Bluephase, Ivoclar Vivadent, Schaan, Liechtenstein) one minute after mixing. The irradiance of the used curing unit ( $=1435 \text{ mW/cm}^2$ ) was determined by means of a calibrated fiber optic spectrally resolving radiometer equipped with an integrating sphere (S2000, Ocean Optics, USA). Total irradiance was achieved by integral calculus of irradiance as a function of wavelength over the entire wavelength range, and then divided by the effective area of the curing unit tip. The diameter of the tip was measured with a digital micrometer, whereby the effective area was defined as the area of the tip without cladding.

The mould was permanently located on the heater for 20 minutes. Then the samples were carefully removed from the mould and stored one week, one month and three months in distilled water at 37°C in order to simulate clinical conditions. The distilled water was changed twice a week, keeping the volume of water constant. The five GICs were thus measured at three different heat conditions (no

heat, 20 s and 60 s heat application) and three different storage durations (one week, one month and three months) making a total of 45 groups ( $n = 10$ ).

After the storage period, the top surface of the samples was polished with silicon carbide paper of grain P2500 and P4000 (Hermes, Virginia Beach, VA, USA). So, a surface layer of approximately 100  $\mu\text{m}$  was eliminated to allow a comparison with real clinical conditions, since in patients, after the cement is cured, the filling must also be polished. In the universal hardness test, the Vickers Hardness, indentation modulus and creep were recorded. The measuring system (Fischerscope H100C, Fischer, Sindelfingen, Germany) used for this study is designed to measure the universal hardness according to DIN 50359-1:1997-10 (Testing of metallic materials-universal hardness test-part 1: test method). In the test, a square diamond indenter in shape of a pyramid (Vickers pyramid) with an opening angle of  $136^\circ$  was pressed vertically into the surface of the specimens. The measurements were carried out force controlled, during which the test load increased and decreased with constant speed between 0 mN and 500 mN. During the test procedure, value pairs of load and penetration depth of the indenter were continuously recorded during both loading and unloading. Due to the known geometry of the Vickers pyramid, the universal hardness [HU] was calculated by the quotient of the test load [F] and the indentation surface [A] generated under load:  $HU = F/A$ . A conversion factor between universal hardness and Vickers Hardness was calculated by the manufacturer and fed into a software (WIN-HCU®, Fischer, Sindelfingen, Germany), so that the measured results were converted into the more common Vickers Hardness units. The elastic indentation modulus, which matches the modulus of elasticity, was determined from the slope of the tangent of indentation depth curve at a maximum force of 500 mN. While constantly holding the maximum test load for five seconds, the relative indentation depth changes were used as a measure for creep. Six different areas on the surface of each sample were measured making a total of 60 measurements in each group.

### *Statistical analysis*

The normal distribution of the data was verified with the Kolmogoroff-Smirnov test. A multivariate analysis (general linear model with partial eta-squared statistics) calculated the effect of the parameters “material”, “heat application” and “storage” on the considered mechanical properties. Additionally, the influence of the parameters “heat application”, “storage” and their combined effect

on the mechanical properties was assessed within each tested material. The level of significance was set at  $p < 0.05$ .

#### *Light microscope and scanning electron microscopy (SEM) analysis*

When measuring the micro-mechanical properties, the surface of all specimens was analysed in the light microscope of the universal hardness device. The size and number of voids and cracks were examined. After the universal hardness test, the top surface of one randomly selected specimen of each GICs group (without heat application, three months storage) was observed in an electronic microscope (scanning electron microscopy SEM, Zeiss Supra 55 VP, Carl Zeiss AG, Oberkochen, Germany) to assess filler size and morphology. For examination, a back-scattered electron image and a standardized magnification of  $1000\times$  was used (Figs 1a-1e). The size and amount of the glass fillers in the matrix were examined to investigate the effects of microstructure on the mechanical properties.

## **Results**

#### *Vickers Hardness, indentation modulus and creep*

In the universal hardness test (Table 2), the mean values of Vickers Hardness varied between 115.6 N/mm<sup>2</sup> (Equia, three months) and 58.7 N/mm<sup>2</sup> (ChemFil Rock, one week). In the ranking of the mean values of indentation modulus, Ketac Molar Aplicap reached the highest value of 28.5 GPa (one month), while ChemFil Rock reached the lowest value of 17.4 GPa (one week). Also in this test, ChemFil Rock distinguished with 4.9 % (one week) the highest mean value of creep and thus the worst creep resistance. The other extreme is Riva Self Cure with 3.5 % (three months).

**Table 2** Micro-mechanical properties: Vickers Hardness (**VH**, N/mm<sup>2</sup>), indentation modulus (**E**, GPa) and creep (**Cr** at 500 mN, %). Mean values and standard deviations (in parentheses)

#### **VH**

<b>Material</b>	<b>Storage</b>	<b>No heat</b>	<b>20 s heat application</b>	<b>60 s heat application</b>
ChemFil Rock	1 week	58.7 (3.4)	60.3 (5.3)	62.1 (3.7)
	1 month	69.7 (5.7)	71.7 (6.0)	69.2 (3.6)
	3 months	71.8 (7.1)	71.6 (5.3)	67.9 (5.0)
Riva Self Cure	1 week	105.1 (7.1)	96.8 (5.6)	93.7 (6.2)
	1 month	99.3 (9.0)	105.7 (8.3)	105.7 (5.2)
	3 months	101.1 (7.3)	99.6 (8.8)	98.6 (4.5)

<b>Material</b>	<b>Storage</b>	<b>No heat</b>	<b>20 s heat application</b>	<b>60 s heat application</b>
Fuji IX GP Fast	1 week	104.6 (7.6)	105.5 (8.4)	106.2 (7.7)
	1 month	107.9 (10.1)	112.2 (8.9)	108.5 (13.3)
	3 months	110.0 (8.9)	108.6 (10.4)	106.6 (10.0)
Fuji IX GP Extra/Equia	1 week	98.1 (7.9)	95.8 (4.8)	96.7 (12.0)
	1 month	108.8 (5.7)	107.4 (4.6)	110.7 (7.9)
	3 months	115.6 (12.4)	110.2 (6.5)	104.6 (6.4)
Ketac Molar Aplicap	1 week	104.6 (4.9)	103.7 (3.3)	102.2 (4.7)
	1 month	110.9 (4.2)	112.5 (11.7)	111.1 (3.2)
	3 months	101.0 (9.5)	99.5 (9.4)	89.5 (7.6)

## E

<b>Material</b>	<b>Storage</b>	<b>No heat</b>	<b>20 s heat application</b>	<b>60 s heat application</b>
ChemFil Rock	1 week	17.5 (1.2)	17.4 (1.0)	17.4 (1.0)
	1 month	19.3 (1.0)	18.4 (1.5)	18.9 (1.0)
	3 months	20.4 (1.7)	20.3 (1.1)	19.7 (1.0)
Riva Self Cure	1 week	24.0 (0.9)	23.1 (0.9)	22.1 (1.5)
	1 month	23.4 (1.3)	22.8 (1.1)	23.2 (1.0)
	3 months	23.6 (2.1)	24.0 (1.4)	23.0 (2.0)
Fuji IX GP Fast	1 week	24.7 (1.0)	24.9 (0.8)	24.9 (1.3)
	1 month	24.8 (1.7)	25.6 (1.5)	24.5 (1.4)
	3 months	26.7 (1.8)	26.0 (1.5)	26.2 (2.2)
Fuji IX GP Extra/Equia	1 week	21.4 (1.3)	20.7 (0.6)	21.0 (1.4)
	1 month	22.3 (0.5)	22.2 (1.1)	22.8 (1.3)
	3 months	24.2 (1.2)	23.3 (1.2)	22.9 (0.6)
Ketac Molar Aplicap	1 week	26.8 (1.1)	26.9 (0.8)	27.2 (1.0)
	1 month	28.5 (0.8)	28.0 (1.0)	28.4 (1.1)
	3 months	27.5 (2.2)	27.0 (2.6)	23.9 (2.3)

## Cr

<b>Material</b>	<b>Storage</b>	<b>No heat</b>	<b>20 s heat application</b>	<b>60 s heat application</b>
ChemFil Rock	1 week	4.9 (0.2)	4.9 (0.3)	4.8 (0.2)
	1 month	4.6 (0.2)	4.6 (0.2)	4.4 (0.1)
	3 months	4.5 (0.2)	4.5 (0.3)	4.5 (0.2)
Riva Self Cure	1 week	3.7 (0.2)	3.8 (0.3)	3.8 (0.2)
	1 month	3.6 (0.2)	3.5 (0.2)	3.7 (0.3)
	3 months	3.5 (0.2)	3.6 (0.2)	3.5 (0.1)
Fuji IX GP Fast	1 week	4.1 (0.3)	4.2 (0.3)	4.0 (0.3)
	1 month	3.8 (0.3)	3.6 (0.2)	3.7 (0.2)
	3 months	3.9 (0.4)	3.9 (0.2)	3.9 (0.2)
Fuji IX GP Extra/Equia	1 week	4.1 (0.2)	4.1 (0.3)	4.1 (0.2)
	1 month	3.8 (0.2)	3.8 (0.2)	3.8 (0.3)
	3 months	3.7 (0.3)	4.0 (0.3)	3.8 (0.1)
Ketac Molar Aplicap	1 week	4.0 (0.2)	4.0 (0.2)	3.9 (0.2)
	1 month	4.0 (0.2)	3.9 (0.3)	3.9 (0.1)
	3 months	4.0 (0.2)	4.2 (0.1)	4.2 (0.1)

*Influence of material, heat application and storage on Vickers Hardness, indentation modulus and creep*

The multivariate analysis indicated that the material showed the highest influence on the micro-mechanical properties (Table 3), followed by the storage duration, whereas heat application showed no influence on creep and a minimum influence on Vickers Hardness and indentation modulus.

**Table 3** Influence of material, heat application and storage on Vickers Hardness (VH), indentation modulus (E) and creep (Cr)

	<b>VH</b>	<b>E</b>	<b>Cr</b>
Material	0.82	0.83	0.71
Heat application	0.02	0.03	NS
Storage	0.17	0.14	0.19

The higher the partial eta-squared values, the higher is the influence of the selected variables on the measured properties (General linear model ( $\eta^2$ )); NS = nonsignificant

*Influence of heat application, storage and their combined effect within a material*

The influence of the parameter heat application was analysed in a general linear model and shown to be significant only in few cases: for the indentation modulus of Riva Self Cure and the Vickers Hardness and indentation modulus of Ketac Molar Aplicap (Table 4). The storage time affected mostly the micro-mechanical properties of the materials ChemFil Rock, Equia and Ketac Molar Aplicap, reaching the highest values for eta-squared.

**Table 4** Influence of heat application, storage and their combined effect on Vickers Hardness (VH), indentation modulus (E) and creep (Cr) within a material

<b>Material</b>	<b>Parameter</b>	<b>VH</b>	<b>E</b>	<b>Cr</b>
ChemFil Rock	Heat application	NS	NS	NS
	Storage	0.48	0.49	0.35
	Heat application + Storage	NS	NS	NS
Riva Self Cure	Heat application	NS	0.07	NS
	Storage	0.09	NS	0.17
	Heat application + Storage	0.18	NS	NS
Fuji IX GP Fast	Heat application	NS	NS	NS
	Storage	NS	0.18	0.32
	Heat application + Storage	NS	NS	NS
Fuji IX GP Extra/Equia	Heat application	NS	NS	NS
	Storage	0.38	0.49	0.26
	Heat application + Storage	NS	NS	NS

Material	Parameter	VH	E	Cr
Ketac Molar Aplicap	Heat application	0.09	0.09	NS
	Storage	0.45	0.26	0.15
	Heat application + Storage	NS	0.23	0.16

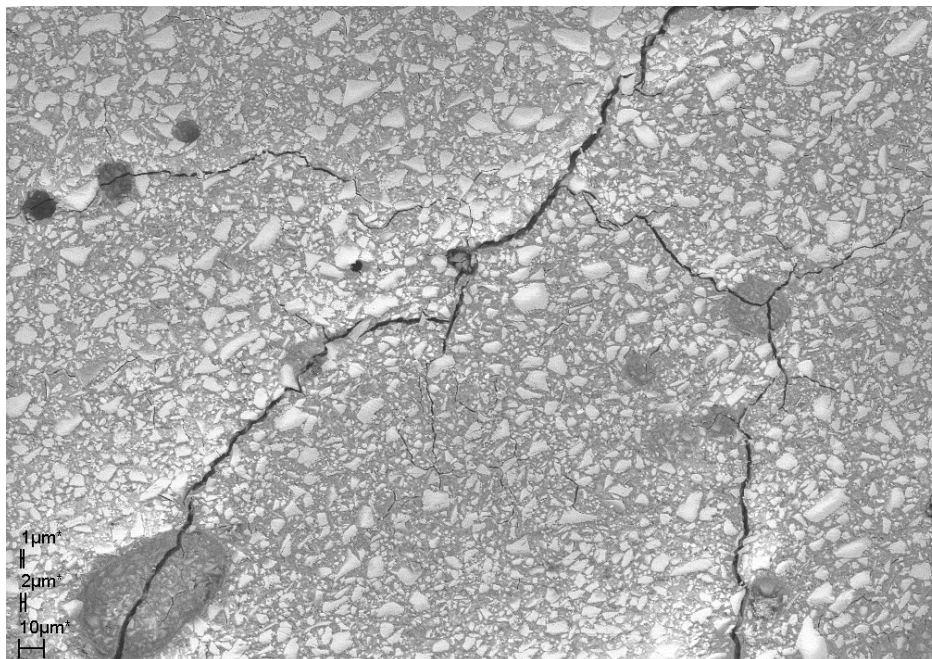
The higher the partial eta-squared values the higher is the influence of the selected variables on the measured properties (General linear model ( $\eta^2$ )) NS = nonsignificant

### *Light microscope and SEM analysis*

Comparing the samples in the light microscope of the universal hardness device, cracks and voids were observed within the matrix of all cements. The void size was greater and more irregular for ChemFil Rock and Riva Self Cure than for Equia, Fuji IX GP Fast and Ketac Molar Aplicap. The smallest void size was observed in the microstructure of Ketac Molar Aplicap. In the SEM, large glass filler particles were detected in the microstructures of Riva Self Cure, Equia and Fuji IX GP Fast. ChemFil Rock and Ketac Molar Aplicap contained many small glass particles dispersed in the matrix.

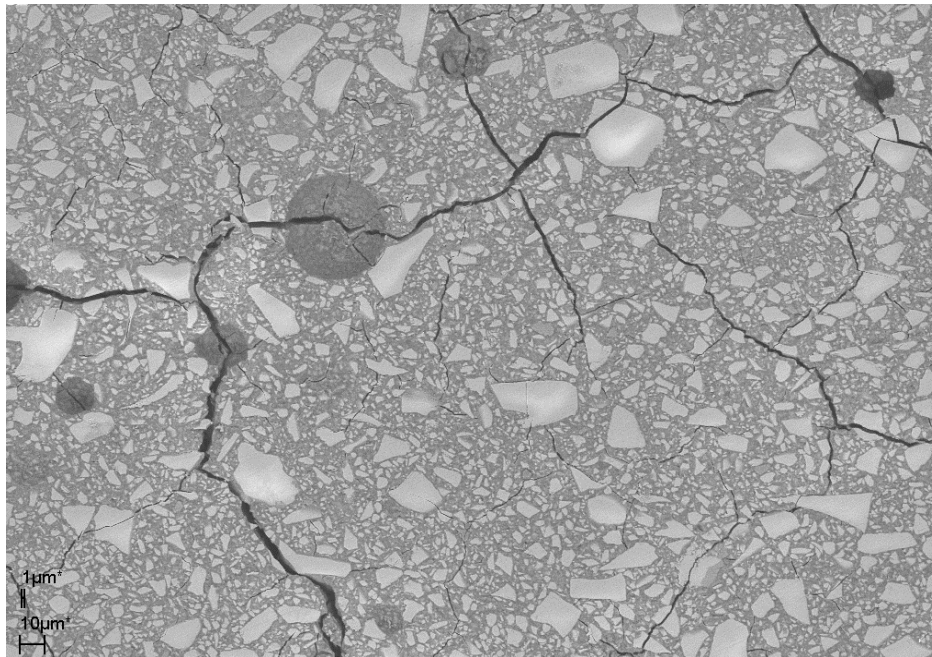
**Figure 1** SEM views of the cements (back-scattered electron image and a standardized magnification of 1000<sup>x</sup>)

a) ChemFil Rock

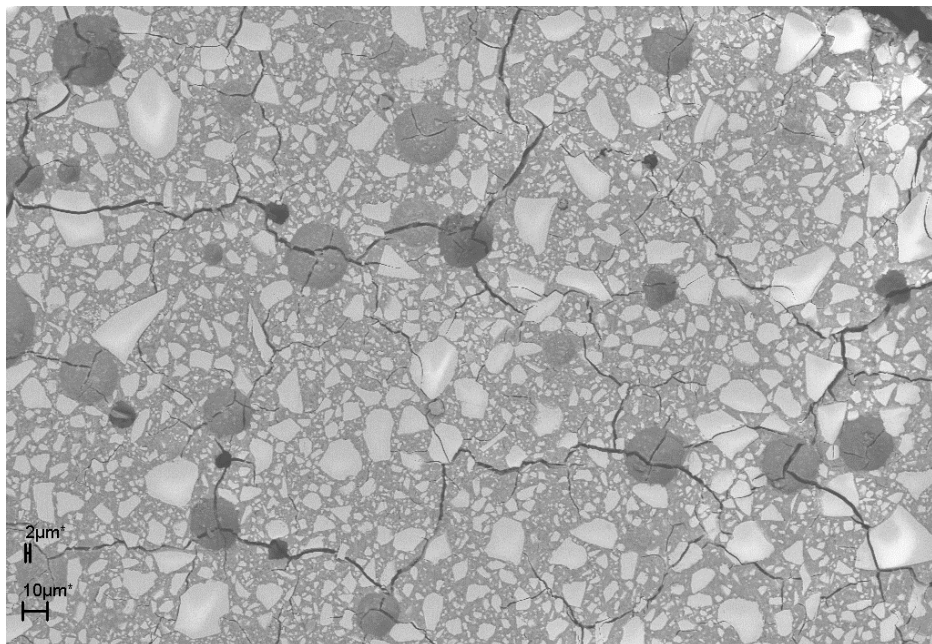




b) Riva Self Cure

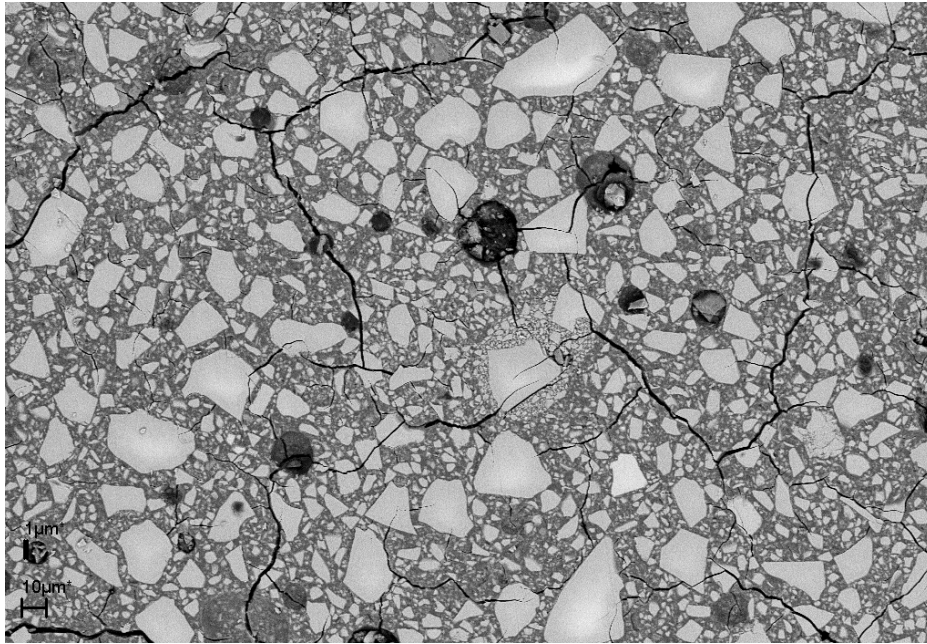


c) Fuji IX GP Fast

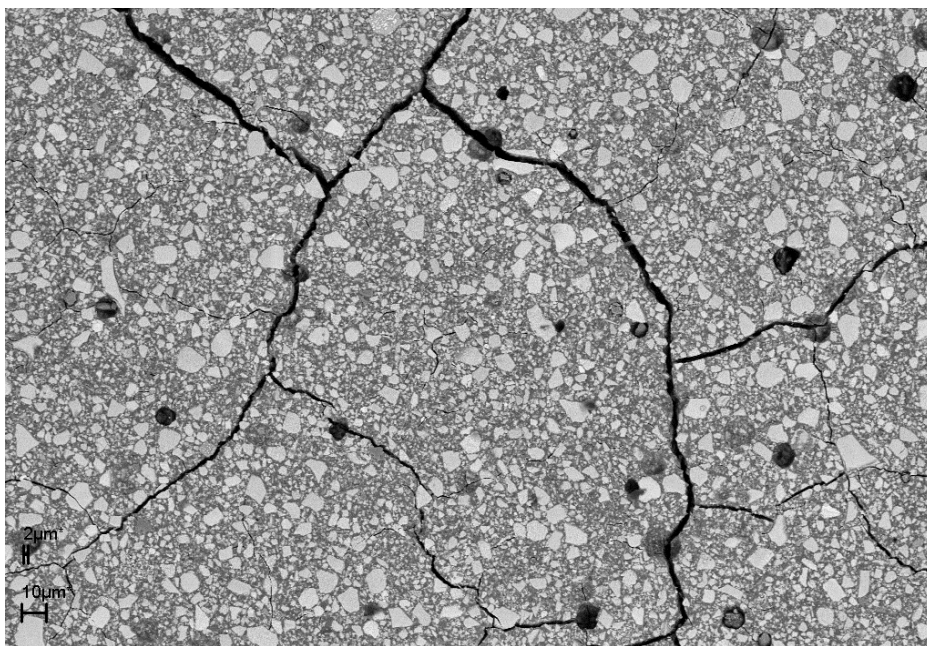




d) Fuji IX GP Extra/Equia



e) Ketac Molar Aplicap



## Discussion

This study evaluated the long-term effect of heat on the micro-mechanical properties of five GICs. Heat application did not influence the mechanical behaviour of ChemFil Rock, Fuji IX GP Fast and Equia at all aging time. The mechanical properties were basically influenced by the type of cement. The impact of storage duration was low. Woolford assumed that heat application is supposed to accelerate the matrix-forming reaction of the cement and so at initial stage the setting reaction will

result in a more advanced and greater surface hardness [2]. GICs contain different aluminosilicate glasses and acids (Table 1). The effect of heat on the setting reaction is supposed to make the acid more active and thus may more rapidly degrade the glass fillers [2]. This causes an increase of the diffusion rate at which the ions are leached and released from the glass [2]. Subsequently, a more reactive acid and greater rate of ion release and diffusion lead to a faster formation of the calcium polyacrylate matrix, the result of the first setting reaction and so to superior mechanical properties [2]. Applying heat improves the early properties of the GICs at a time when they are most susceptible to damage. Heat application enhances the reaction rate [2, 17] but does not change the mechanical properties of the GICs. It just accelerates the first setting reaction but in our study no long-term effect was observed. The small significant difference of the Vickers hardness and modulus of elasticity of Riva Self Cure and Ketac Molar Aplicap treated by different heat conditions can be attributed to incorrect measurements and varying temperature conditions even though they were tried to keep constant.

Previous studies showed that the use of an external energy source such as preheating capsules ( $40 \pm 1^\circ\text{C}$  for 90 s prior to activation), application of light with a high irradiance (halogen light-curing unit: Optilux 501, Kerr UK Ltd., Peterborough, United Kingdom; operating at  $1012 \pm 20 \text{ mW cm}^{-2}$  for 40 s) or ultrasonic energy (P-tip ultrasonic scaler driven by Mini-Piezon US generator, EMS, Nyon, Switzerland; operating at 30 kHz, power setting 1 for 40 s) significantly improved the early surface hardness of GIC (0.5 h post-mix) compared to the standard setting reaction [22]. Also, Chemfil II (DeTrey Division, Dentsply, Weybridge, Surrey, United Kingdom) heated under an infrared light source (Phillips Electrical, Holland; operating at  $80^\circ\text{C}$  for 60 s) and a quartz halogen fibre optic light source (Litema GSD, Baden-Baden, Germany; operating for 20, 40 and 60 s) showed a significant increase in hardness immediately after setting and 24 h post-mix in comparison to the cement which had not been heat treated [2].

The most common available light curing units include quartz-tungsten-halogen (QTH) lights, plasma arc lights and LEDs [23]. For many years QTH lights became the mainstay of dental light curing [24]. However, the future of the QTH lights will be poor as no light bulbs are produced any more and many governmental agencies are banning these inefficient incandescent light sources from general

usage [24]. Therefore, in our study the heat was applied by a LED curing unit (irradiance: 1435 mW/cm<sup>2</sup>). The LED light curing units can be classified into three generations based on successive improvements of their performance [25]. First-generation LED (average irradiance: 150-400 mW/cm<sup>2</sup>, power output 1W) offer low output and poor curing performance compared to conventional QTH lights [23]. Second-generation LED (irradiance of up to 800 mW/cm<sup>2</sup>, power output 5 W) [23] can achieve superior polymerization and curing performances which are similar to those of QTH lights under equal exposure times [26]. Third-generation LED lights (exceed 1100 mW/cm<sup>2</sup>, power output 8 W) [27] use a combination of LEDs to produce a broader spectral output [23]. They have higher power densities, inducing potentially higher heat emissions and curing depths and perform as well as or even better than QTH lights [23, 28]. Earlier studies indicated that LED curing units generally generated smaller temperature rises than QTH units [23, 26]. However these studies used first-generation LED curing units, which have lower power than some of the second- and third-generation LED curing units used today [23, 26]. Previous studies concluded that second- and third-generation LED lights (L.E. Demetron 1, SDS/Kerr, Orange, CA, USA and Blue Phase C5, Ivoclar Vivadent, Inc., Amherst, NY, USA) generated the same or similar heat emissions and temperature rises than QTH lights (VIP, Bisco, Schaumburg, IL, USA and Cromalux 100, Mega-Physik GmbH & Co., KG, Rastatt, Germany) [18, 23]. This result is different from the use of lower power density LED units [23]. Hence, heat can be applied by a QTH or a high energy LED light, like made in our study.

Ultrasonic excitation is supposed to produce heat and thus to accelerate the setting reaction [20, 29, 30]. But on the other hand, compared to heat application, ultrasonic excitation reduces the void size verifiable and so the porosity of the cements [30]. The macro-mechanical properties, e.g. compressive strength are influenced by voids. A reduced void size in the microstructure of the samples results in improved macro-mechanical properties [31] compared to samples without ultrasonic excitation. However, the micro-mechanical properties (Vickers Hardness, modulus of elasticity and creep) are less capable of being influenced by ultrasonic excitation and voids, as the measurements occur on selected areas of the surface where few voids are present.

During the first setting reaction, GICs are very susceptible to water contamination which results in inferior mechanical properties [15]. Thus, the cements have to be protected by a surface coating to

maintain water balance of the restorations [15]. In our study during the first 20 minutes of the setting reaction transparent matrix strips were used to simulate the coating and protect the cements from loss or gain of moisture. Since the storage medium water or artificial saliva was proved not to be a significant factor affecting the mechanical properties of GICs [32], the samples were stored in our study in distilled water. As cracks were observed on the surface of all one week stored samples after the universal hardness test, new samples from the same batch were prepared for the one month and three months measurements. The cracks were caused by dehydration during the microhardness test. In this study the cements were polished right before the universal hardness test to simplify the test procedure. Statistically, resin modified GICs showed no significant difference in hardness means recorded at four analysed depths (up to 2.6 mm) [33]. A fact that can possibly be explained by the continuing acid-base reaction and a chemical-free radical polymerization after the removal of the light-source and therefore ensure a complete hardening of the material [33]. Also no effect of the storage medium on the mechanical properties was observed [32]. Hence, it can be concluded that the measured mechanical properties do not depend on a particular polishing time or depth.

Comparing the differences of the mechanical properties within a material at varying storage times, the small differences can be partially attributed to incomplete setting after one week compared to one or three months. Previous studies reported that the hardness of GICs (e.g. Fuji IX GP) was significantly lower at one day than at one week and one month [21]. The hardening process occurs after the gelation phase and involves an increase in strength due to the continued formation of aluminium salt bridges and increase in the ratio of bound to unbound water [34]. Storage strengthens the matrix of the cements and thus, leads to superior mechanical properties. However, long-term storage can result in a decrease in strength as a result from erosion and plasticizing effect of water [35]. Tartaric acid - contained in Riva Self Cure and Ketac Molar Aplicap - increases the stability of the cements [36]. Tartaric acid acts as an accelerator that effectively increases the amount of aluminium which is released from the glass [36]. So, tartaric acid accelerates the final setting reaction. This fact, revealed in our study, as the parameter “storage” showed no or just a small significant influence on the mechanical properties of Riva Self Cure. A high mean value was already achieved after one week and stayed at a nearly constant value during three months storage.

Examining and comparing the microstructures, compositions and mechanical properties of cements some relationships were detected. The setting reaction and subsequent mechanical properties of GICs are influenced by the filler size and distribution in the matrix. Small filler sizes in GICs increase the surface area and provide a greater surface area for acid attack, thereby reducing the setting time [37]. In this study small glass particles were observed in the microstructure of Chemfil Rock and Ketac Molar Aplicap but their mechanical behaviours differed significantly. This may be due to the different void size and the chemical composition (Table 1). The calcium-aluminium-zinc-fluoro-phosphor-silicate glass of ChemFil Rock seems less strong than the calcium-aluminium-lanthanum-fluorosilicate glass of Ketac Molar Aplicap. According to the manufacturer, the zinc-containing glass of ChemFil Rock should accelerate the setting reaction of the GIC and thus lead to a higher strength. Previous studies revealed superior macro-mechanical properties (e.g. flexural strength) for ChemFil Rock compared to Riva Self Cure, Fuji IX GP Fast and Equia after one week and month [32]. However, ChemFil Rock showed the lowest values in Vickers hardness and modulus of elasticity [32]. So, the zinc-containing GIC ChemFil Rock is inferior in the micro-mechanical properties compared to the aluminosilicate glass cements tested. In our study the void size does not influence the micro-mechanical properties as measurements were accomplished on areas of the specimens with less voids. Previous studies approved that Ketac Molar Easymix (3M ESPE, Seefeld, Germany) and Fuji IX (GC Europe N.V., Leuven, Belgium) performed better in the mechanical properties (wear resistance, Knoop hardness, flexural and compressive strength) compared to Riva Self Cure after 24 hours [38].

## **Conclusions**

Statistical analysis revealed that heat application showed no effect on the mechanical behaviour of ChemFil Rock, Fuji IX GP Fast and Equia at all aging time. The mechanical properties were basically influenced by the type of cement. The impact of storage duration was low. Vickers Hardness, modulus of elasticity and creep resistance increased most for ChemFil Rock and Equia up to one month storage.

## **Conflict of interest**

The authors declare that they have no conflicts of interest.

## References

1. Talal A, Tanner KE, Billington R, Pearson GJ (2009) Effect of ultrasound on the setting characteristics of glass ionomer cements studied by Fourier Transform Infrared Spectroscopy. *J Mater Sci Mater Med* 20:405-411
2. Woolford MJ (1994) Effect of radiant heat on the surface hardness of glass polyalkenoate (ionomer) cement. *J Dent* 22:360-363
3. Sidhu SK (2010) Clinical evaluations of resin-modified glass-ionomer restorations. *Dent Mater* 26:7-12
4. Wiegand A, Buchalla W, Attin T (2007) Review on fluoride-releasing restorative materials - fluoride release and uptake characteristics, antibacterial activity and influence on caries formation. *Dent Mater* 23:343-362
5. Mazzaoui SA, Burrow MF, Tyas MJ (2000) Fluoride release from glass ionomer cements and resin composites coated with a dentine adhesive. *Dent Mater* 16:166-171
6. Sidhu SK (2011) Glass-ionomer cement restorative materials: a sticky subject? *Austr Dent J* 56:23-30
7. Kleverlaan CJ, Van Duinen RNB, Feilzer AJ (2004) Mechanical properties of glass ionomer cements affected by curing methods. *Dent Mater* 20:45-50
8. Manhart J, Garcia-Godoy F, Hickel R (2002) Direct posterior restorations: clinical results and new developments. *Dent Clin N Am* 46:303-339
9. Manhart J, Chen H, Hamm G, Hickel R (2004) Review of the clinical survival of direct and indirect restorations in posterior teeth of the permanent dentition. *Oper Dent* 29:481-508
10. Hickel R, Manhart J (2001) Longevity of restorations in posterior teeth and reasons for failure. *J Adhes Dent* 3:45-64
11. Zanata RL, Fagundes TC, Freitas MC, Lauris JR, Navarr MF (2011) Ten-year survival of ART restorations in permanent posterior teeth. *Clin Oral Invest* 15:265-271
12. Mahoney E, Kilpatrick N, Johnston T (2008) Restorative paediatric dentistry. In: Cameron AC, Widmer RP (ed) *Handbook of Pediatric Dentistry*, 3rd edn. Mosby, Maryland Heights, pp 71-93



13. Barry TI, Clinton DJ, Wilson AD (1979) The structure of a glass-ionomer cement and its relationship to the setting process. *J Dent Res* 58:1072-1079
14. Mount GJ (1999) Glass ionomers: a review of their current status. *Oper Dent* 24:115-124
15. Hattab FN, Amin WM (2001) Fluoride release from glass ionomer restorative materials and the effects of surface coating. *Biomaterials* 22:1449-1458
16. Frankenberger R, Garcia-Godoy F, Krämer N (2009) Clinical Performance of Viscous Glass Ionomer Cement in Posterior Cavities over Two Years. *Int J Dent*. doi: 10.1155/2009/781462
17. Algera TJ, Kleverlaan CJ, Prahl-Andersena B, Feilzer AJ (2006) The influence of environmental conditions on the material properties of setting glass-ionomer cements. *Dent Mater* 22:852-856
18. Vandewalle KS, Roberts HW, Tiba A, Charlton DG (2005) Thermal emission and curing efficiency of LED and halogen curing lights. *Oper Dent* 30:257-264
19. Woolford MJ, Grieve AR (1995) Release of fluoride from glass polyalkenoate (ionomer) cement subjected to radiant heat. *J Dent* 23:233-237
20. Carvalho CA, Fagundes TC, Barata TJ, Navarro MF (2008) Influence of ultrasonic setting on microhardness of glass-ionomer cements. *J Minim Interv Dent* 1:66-76
21. Yap AUJ, Cheang PHN, Chay PL (2002) Mechanical properties of two restorative reinforced glass-ionomer cements. *J Oral Rehabil* 29:682-688
22. O'Brien T, Shoja-Assadi F, Lea SC, Burke FJT, Palin WM (2010) Extrinsic energy sources affect hardness through depth during set of a glass ionomer cement. *J Dent* 38:490-495
23. Wahbi MA, Aalam FA, Fatiny FI, Radwan SA, Eshan IY, Al-Samadani KH (2012) Characterization of heat emission of light-curing units. *Saudi Dent J* 24:91-98
24. Rueggeberg FA (2011) State-of-the-art: Dental photocuring—A review. *Dent Mater* 27:39-52
25. Rueggeberg FA, Blalock JS, Callan RS (2005) LED curing lights - what's new? *Compend Contin Educ Dent* 26:586-591
26. Asmussen E, Peutzfeldt A (2005) Temperature rise induced by some light emitting diode and quartz-tungsten-halogen curing units. *Eur J Oral Sci* 113:96-98
27. Pérez M, Pérez-Ocón F, Lucena-Martín C, Pulgar R (2008) Stability and Reproducibility of Radiometric Properties of Light Curing Units (LCUs). Part II: LED LCUs. *Dent Mater J* 27:292-299

28. Price RB, Felix CA, Andreou P (2005) Evaluation of a dual peak third generation LED curing light. *Compend Contin Educ Dent* 26:331-347
29. Algera TJ, Kleverlaan CJ, Gee AJ, Prah-Andersen B, Feilzer AJ (2005) The influence of accelerating the setting rate by ultrasound or heat on the bond strength of glass ionomers used as orthodontic bracket cements. *Eur J Orthod* 27:472-476
30. Coldebella CR, Santos-Pinto L, Zuanon ACC (2011) Effect of Ultrasonic Excitation on the Porosity of Glass Ionomer Cement: A Scanning Electron Microscope Evaluation. *Microsc Res and Tech* 74:54-57
31. Xie D, Brantley WA, Culbertson BM, Wang G (2000) Mechanical properties and microstructures of glass-ionomercements. *Dent Mater* 16:129-138
32. Zoergiebel J, Ilie N (2013) Evaluation of a conventional Glass Ionomer Cement with new zinc formulation: Effect of coating, aging and storage agents. *Clin Oral Invest* 17:619-626
33. Palma-Dibb RG, Palma AE, Matson E, Chinelatti MA, Ramos RP (2002) Microhardness of esthetic restorative materials at different depths. *Mat Res* 6:85-90
34. Nicholson JW (1998) Chemistry of glass-ionomer cements: a review. *Biomaterials* 19:485-494
35. Cattani-Lorente MA, Godin C, Meyer JM (1994) Mechanical behavior of glass ionomer cements affected by long-term storage in water. *Dent Mater* 10:37-44
36. Crisp S, Wilson AD (1976) Reactions in Glass Ionomer Cements: V. Effect of Incorporating Tartaric Acid in the Cement Liquid. *J Dent Res* 55:1023-1031
37. Tanner DA, Rushe N, Towler MR (2006) Ultrasonically set glass polyalkenoate cements for orthodontic applications. *J Mater Sci Mater Med* 17:313-318
38. Bonifácio CC, Kleverlaan CJ, Raggio DP, Werner A, de Carvalho RC, van Amerongen WE (2009) Physical-mechanical properties of glass ionomer cements indicated for atraumatic restorative treatment. *Austr Dent J* 54:233-237



## **2.2. Effect of gloss and heat on the mechanical behaviour of a glass carbomer cement**

### **Abstract**

*Objectives:* The effect of gloss and heat on the mechanical behaviour of a recently launched glass carbomer cement (GCP, GCP dental) was evaluated and compared with resin-modified glass ionomer cements (Fuji II LC, GC and Photac Fil Quick Aplicap, 3M ESPE).

*Methods:* 120 bar-shaped specimens (n=20) were produced, maintained in distilled water at 37°C and tested after one week. The GCP specimens were cured with and without heat application and with and without gloss. The flexural strength and modulus of elasticity in flexural test as well as the micro-mechanical properties (Vickers Hardness, indentation modulus, creep) of the top and bottom surface were evaluated. The amount and size of the fillers, voids and cracks were compared using a light and a scanning electron microscope.

*Results:* In the flexural test, the resin-modified glass ionomer cements performed significantly better than GCP. Fuji II LC and Photac Fil (Weibull parameter: 17.7 and 14.3) proved superior reliability in the flexural test compared to GCP (1.4 - 2.6). The highest Vickers Hardness and lowest creep were achieved by GCP, whereas Fuji II LC reached the highest indentation modulus. The results of this study proved that relationships exist between the compositions, microstructures and mechanical properties of the cements.

*Conclusions:* Heat treatment and gloss application did not influence the mechanical properties of GCP. The mechanical properties were basically influenced by the type of cement and its microstructure.

*Clinical significance:* Considering the measured mechanical properties, there is no need of using gloss or heat when restoring teeth with GCP.

### **Introduction**

During the last few years, a new glass ionomer-based restorative material had been developed: glass carbomer. GCP is a fluorapatite-containing glass carbomer cement with powder particles reduced to nano size.<sup>1</sup> GCP and its clinical application are similar to conventional glass ionomer cements (cGICs), except that heat application is recommended during the setting reaction. According to the manufacturer GCP sets chemically and is optimised for heat curing. The appendent GCP gloss is a

silicone-based coat to protect the surface from exposure to moisture and saliva during the first setting reaction and from dehydration in the second phase. Thus, the manufacturer claims that it leads to superior product characteristics.

GICs are mainstream restorative materials used for lining, bonding, luting, sealing or restoring a tooth.<sup>2</sup> CGICs are acknowledged for their chemical bonding to enamel and dentine, continuing fluoride release and show no setting shrinkage under clinical conditions.<sup>3, 4</sup> On the other hand, it is subject to criticism due to its lack of physical strength especially in the initial stage of setting, the slow curing reaction and moisture sensitivity.<sup>2</sup> Therefore, the low mechanical properties of existing cGICs make them unsuitable for use in high stress-bearing areas, such as posterior teeth.<sup>5</sup> However, several studies recommend, the use of highly viscous cGICs placed in single-surface posterior permanent teeth by means of the atraumatic restorative treatment (ART) approach<sup>6</sup> but also in primary teeth.<sup>7</sup> Fatigue fractures after several years of clinical service are a usual cause of failure in GIC restorations.<sup>8</sup> Moreover, the median annual failure rate in posterior stress-bearing cavities was shown to be high for glass ionomer cements (7.7%) when compared to amalgam (1.1%) or direct resin-based composite restorations (2.1%).<sup>9</sup>

The quest for a perfect restorative filling material has been ongoing. Efforts for improvement of cements had been made in several aspects: metal particles were added (e.g. Ketac Silver, 3M ESPE, Seefeld, Germany), resin-modified glass ionomer cements (RMGICs) were introduced in 1992, the viscosity was increased by reducing filler size (e.g. Ketac Molar, 3M ESPE, Seefeld, Germany) and recently, glass carbomer cement had been developed.<sup>10, 11</sup> Furthermore, the incorporation of nanoparticles (nanohydroxyapatite and nanofluorapatite) into cGICs showed an improve of their mechanical behaviour and bond strength to dentine.<sup>12</sup> Compared to cGICs, RMGICs are characterised by having a longer working time, a rapid set, improved aesthetic appearance and translucency and an increased early strength.<sup>13, 14</sup> The longevity and strength of cements partly depend on their mechanical properties. Although the mechanical properties do not necessarily represent the cements' actual clinical performance, they are used to guide the effects of changes in the composition or application or processing on these properties.<sup>15</sup> Furthermore, laboratory and in vivo tests might help the clinician to

choose the right material once comparisons between former formulations and new ones, as well as, with the leading brand, are highlighted.<sup>15</sup>

Besides, in order to improve the mechanical properties application of ultrasonic or heat energy to cGICs can be used so that the cement sets “on command”.<sup>16</sup> The compressive strength of heat treated cGICs showed an increase compared to the standard setting reaction of the material at early curing time.<sup>16</sup> An obvious relationship between temperature of the samples and compressive strength of cGICs was measured.<sup>16</sup> It was observed that raising the temperature of the surface of the cement to a maximum of 60°C significantly improved the surface hardness of the material after 24 hours.<sup>17</sup> Furthermore regarding glass carbomer, the amount of heat is directly associated with the quality of the cement setting.<sup>18</sup> The use of heat is supposed to accelerate the matrix-forming reaction of cGICs<sup>17</sup> and GCP.<sup>19</sup> When using different polymerisation units (e.g. heat) no significant difference in the micro-hardness for the upper and lower surface of the GCP specimens was measured.<sup>17</sup> Further studies about glass carbomer concluded that the retention rate of glass carbomer was comparable to Helioclear F (Ivoclar Vivadent, Ellwangen, Germany) after six months of clinical trial (retention rate: 100% ).<sup>20</sup> Glass carbomer showed lower microleakage values than fast setting cGIC (Fuji IX GP Extra, GC, Leuven, Belgium).<sup>21</sup> Besides, the flexural strength of glass carbomer ( $122.29 \pm 9.9$  MPa) was higher compared to cGICs (Fuji IX GP Fast, GC, Leuven, Belgium ( $57.85 \pm 7.54$  MPa)) after 24 h<sup>22</sup> and GCP showed significantly higher shear bond strength (13.7 MPa) comparing to cGIC (6.7 MPa).<sup>19</sup> Thus, glass carbomer might be a great development and further research is necessary to confirm its mechanical properties. Analysing the compressive strength of teeth restored with RMGIC, GCP and cGICs after three weeks, the compressive strength of the RMGIC teeth was statistically significantly higher than of GCP and cGICs.<sup>23</sup> It was concluded that restorations of GCP were less fracture resistant than those of cGICs.<sup>23</sup>

It is assumed that the heat emitted by a curing unit during polymerisation of a gloss or coating could additionally positively affect the mechanical properties of cements.

The aim of this study was therefore to assess the effect of gloss and heat on the mechanical behaviour of a glass carbomer cement and to compare it with RMGICs. Therefore mechanical properties at

macroscopic (flexural strength and modulus of elasticity in flexural test) and microscopic scale (Vickers Hardness, indentation modulus and creep) were recorded.

The tested null hypotheses were that: i) there would be no difference in the measured properties of the glass carbomer cement when gloss, heat or both factors are applied; ii) glass carbomer cement would perform similarly to the RMGICs in all properties; iii) in all materials no differences in the mechanical properties would be between the top and bottom surface of the 2 mm-specimens.

## Materials and methods

### *Flexural strength and modulus of elasticity in flexural test*

The three cements used are listed in Table 1 (Fuji II LC, Photac Fil Quick Aplicap, GCP), together with the manufacturer, batch number and composition according to the material safety data sheet.

**Table 1** - Material, manufacturer, batch number and chemical composition of the cements.

Material	Manufacturer	Batch no.	Chemical composition
Fuji II LC capsule	GC Europe N.V., Leuven, Belgium	1109107	Alumino-fluorosilicate glass, polyacrylic acid, 2-hydroxyethylmethacrylate, 2,2,4-trimethyl hexamethylene dicarbonate, triethylene glycol dimethacrylate
Photac Fil Quick Aplicap	3M ESPE, Seefeld, Germany	454040	Sodium-calcium-aluminium-lanthanum-fluorosilicate glass, 2-hydroxyethylmethacrylate, difunctional monomers, activator (amine), copolymer of acrylic acid and maleic acids, camphor-quinone stabilisers (radical captors, chelating agents)
GCP Glass fill & gloss GCP 1: no gloss, no heat GCP 2: no gloss, but heat GCP 3: gloss, no heat GCP 4: gloss and heat	GCP Dental, Vianen, the Netherlands	7103067  1104070	Fill: fluoro-aluminosilicate glass, apatite, polyacids gloss: modified polysiloxanes

They were tested in encapsulated form and in shade A3. 120 bar-shaped specimens (16 mm length, 2 mm width, 2 mm height) were produced out of the three cements by using a stainless steel mould which was placed on a heater (Präzitherm PZ 34, Bachofer, Reutlingen, Germany) at 37°C to simulate clinical conditions (n=20). All products were used according to the manufacturers' instructions and mixed for 10 seconds with a RotoMix (3M ESPE, Seefeld, Germany). The mould was filled with

uncured cement and covered with a transparent matrix strip (Matrix-Strips, Orbis, Muenster, Germany) and a glass plate on which a gentle force was applied to eliminate excess material and to achieve possibly void free samples. The mould was permanently located on the heater. The samples were allowed to set for 20 minutes in the mould, then ground with grinding silicon carbide paper of grain P1200 (LECO, St. Joseph, MI, USA) in order to remove excess material and edge defects.

The RMGIC specimens were polymerised from both sides for 20 seconds (LED curing unit, Bluephase, Ivoclar Vivadent, Schaan, Liechtenstein) with three light exposures, overlapping one irradiated section no more than 1 mm of the diameter of the light guide. For the GCP four different curing conditions were used: no gloss and no heat application (GCP 1), no gloss but heat application (GCP 2), gloss but no heat application (GCP 3) and gloss and heat application (GCP 4) (Table 1). The heat was applied from both sides by using the LED curing unit described above for 20 seconds with three heat exposures, overlapping one heated section no more than 1 mm of the diameter of the light guide.

To simulate clinical conditions the samples were stored at 37°C in distilled water for one week and afterwards the flexural strength was determined in a three-point flexural strength test (n=20) according to ISO 4049:2009 (Dentistry - polymer-based restorative materials). The specimens were loaded into a universal testing machine (Zwick/Roell Z 2.5, Ulm, Germany and test Xpert II software) with a constant crosshead speed of 0.5 mm/min until they fractured. During the test, the specimens were immersed in distilled water at room temperature.

Flexural strength  $\sigma$  was calculated from formula (1).

$$(1) \quad \sigma = \frac{3Fl}{2bh^2}$$

F is the maximum load [N], l is the distance between the supports [mm], b is the width of the specimens [mm], h is the height of the specimens [mm].

The universal testing machine stored the force during bending and the deflection of the beam in a file.

The bending modulus  $E_{flexural}$  was calculated from formula (2).

$$(2) \quad E_{flexural} = \frac{Fl^3}{4bh^3_y}$$

Y is the deflection at load point [mm].

#### *Vickers Hardness, indentation modulus and creep*

Randomly selected fragments (n=20) of the specimens tested in the flexural test were directly evaluated in the universal hardness test. Prior to the measurement, the surface of the specimens were ground with grinding silicon carbide paper of grain P2500 and P4000 (Hermes, Virginia Beach, VA, USA). So a surface layer of approximately 100 µm was eliminated. Measurements were made with an automatic microhardness indenter (Fischerscope H100C, Fischer, Sindelfingen, Germany). The Vickers Hardness, indentation modulus and creep of the top and bottom surface were determined (n=10). The measuring system used for this study (Fischerscope H100C) is designed to measure the universal hardness according to DIN 50359-1:1997-2010 (testing of metallic materials-universal hardness test-part 1: test method) by documenting value pairs of load and indentation depth. A diamond indenter in shape of a right pyramid with a square base and an angle  $\alpha = 136^\circ$  between the opposite faces of the vertex (Vickers pyramid) was pressed vertically into the surface of each specimen. The test procedure was carried out force controlled, where the increased and decreased of the test load happened at a constant speed between 0 mN and 500 mN. Value pairs of load and penetration depth of the indenter were continuously recorded during both loading and unloading. Due to the known geometry of the Vickers pyramid, the universal hardness [HU] was calculated by the quotient of the test load [F] and the indentation surface [A] generated under load:  $HU = F/A$ . From a multiplicity of measurements stored in a database supplied by the manufacturer, a conversion factor between universal hardness and Vickers Hardness was calculated and fed into a software (WIN-HCU®, Fischer, Sindelfingen, Germany), so that measurement results were indicated in the more familiar Vickers Hardness units. The elastic indentation modulus, which can be compared to the modulus of elasticity, could be detected from the slope of the tangent of indentation depth curve at a maximum force of 500 mN. While constantly holding the maximal test load for 5 seconds, the changing indentation depth at constant test load indicates the measure for creep. 20 specimens of each

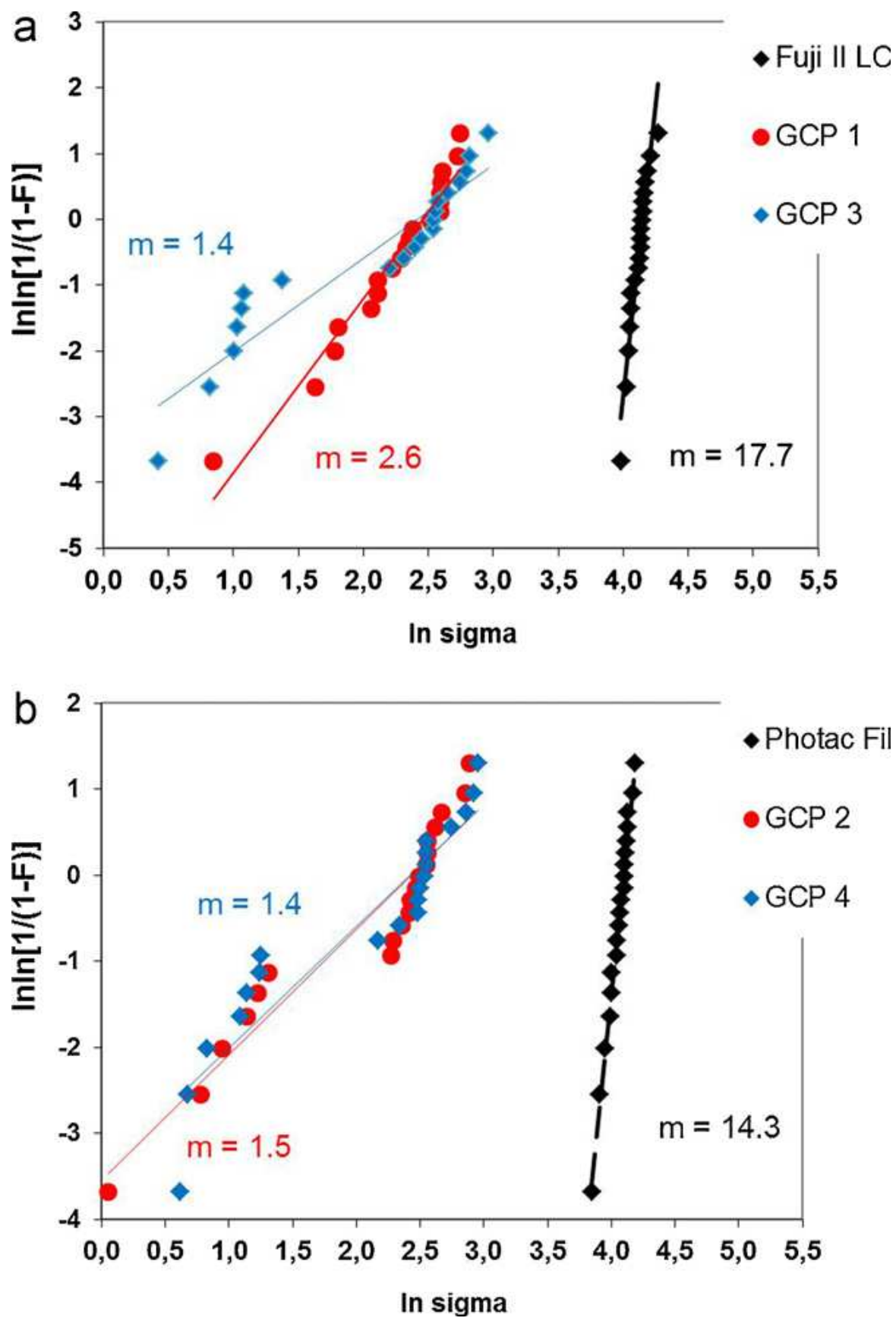
group were examined, 10 times the top and 10 times the bottom surface. Six indentations were accomplished on each specimen making a total of 60 measurements on each surface.

#### *Statistical analysis*

The Kolmogoroff-Smirnoff test was applied to verify if the data was normally distributed. Results were compared using one and multiple-way ANOVA and Tukey HSD post hoc-test ( $\alpha = 0.05$ ). A multivariate analysis (general linear model with partial eta-squared statistics) assessed the effect of the parameters “material” and “surface” on the considered properties. An independent t-test additionally analysed the differences in micro-mechanical properties between the top and bottom of the specimens (SPSS Inc.; Chicago, IL, USA, Version 19.0). Besides a Weibull analysis was performed for the flexural strength data (Fig. 1(a and b)).

**Figure 1** - Weibull analysis for the cements. The Weibull parameter  $m$  is indicated.

(a) Fuji II LC, GCP 1 and GCP 3 and (b) Photac Fil, GCP 2 and GCP 4.





A common empirical expression for the cumulative probability of failure,  $P$ , at applied stress is the Weibull model:

$$P_f(\sigma_c) = 1 - \exp\left[-\left(\frac{\sigma_c}{\sigma_0}\right)^m\right]$$

where  $\sigma_c$  is the measured strength,  $m$  the Weibull modulus and  $\sigma_0$  the characteristic strength, defined as the uniform stress at which the probability of failure is 0.63. The double logarithm of this expression gives:

$$\ln \ln \frac{1}{1-P} = m \ln \sigma_c - m \ln \sigma_0$$

By plotting  $\ln \ln(1/(1-P))$  versus  $\ln \sigma$ , a straight line results, with the upward gradient  $m$ , whereas the intersection with the x-axes gives the logarithm of the characteristic strength.<sup>24</sup>

#### *Light microscope and scanning electron microscopy (SEM) analysis*

When measuring the micro-mechanical behaviour, the surface of all specimens was observed in the light microscope of the universal hardness device. The size and number of voids and cracks were compared. After testing the micro-mechanical properties, the surface of the cements was studied in an electronic microscope (SEM, Zeiss Supra 55 VP, Carl Zeiss AG, Oberkochen, Germany) using a back-scattered electron image. For the examination, one specimen was randomly selected from each cement, mounted on a metallic stub and the upper surface was studied, using a standardised magnification of 5000x (Fig. 2(a-c)). The size, amount and distribution of the glass fillers in the specimens were compared to investigate the effects of microstructure on the mechanical properties.

## **Results**

#### *Flexural strength and modulus of elasticity in flexural test*

In the ranking of the mean values of flexural strength (Table 2) the RMGICs, Fuji II LC and Photac Fil reached the highest values (61.8 MPa, 58.0 MPa), while GCP exhibited only one sixth of the maximum flexural strength of these series (9.5 - 10.1 MPa). Post hoc multiple pairwise comparisons

with Tukey's HSD test ( $p < 0.05$ ) found two clearly separate, homogeneous subgroups. This also proves that GCP offered significant lower means of flexural strength without differences within the four GCP groups. Different results were observed regarding the moduli of elasticity in flexural test. GCP and Fuji II LC offered the highest modulus of elasticity (3.8 - 4.8 GPa), while Photac Fil showed the lowest mean value (2.6 GPa).

**Table 2** - Macro-mechanical properties.

<b>Material</b>	<b>FS</b>	<b>E<sub>flexural</sub></b>	<b>m</b>
Fuji II LC	61.8 <sup>b</sup> (4.2)	4.2 <sup>BC</sup> (0.5)	17.7
Photac Fil	58.0 <sup>b</sup> (4.9)	2.6 <sup>A</sup> (0.8)	14.3
GCP 1	10.1 <sup>a</sup> (3.6)	3.8 <sup>B</sup> (1.0)	2.6
GCP 2	9.7 <sup>a</sup> (5.2)	4.8 <sup>C</sup> (0.7)	1.5
GCP 3	9.7 <sup>a</sup> (5.8)	4.2 <sup>BC</sup> (1.2)	1.4
GCP 4	9.5 <sup>a</sup> (6.1)	4.8 <sup>C</sup> (0.9)	1.4

Flexural strength (FS, MPa) and modulus of elasticity in flexural test (E<sub>flexural</sub>, GPa) in mean values and standard deviations (in parentheses). Superscript letters indicate statistically homogeneous subgroups within a column (Tukey's HSD test,  $\alpha = 0.05$ ). The Weibull parameter m is indicated.

Weibull analysis for the flexural data is listed in Table 2 as well and Fig 1(a and b) show the Weibull analysis for the flexural strength data of the cements. With a Weibull parameter of 17.7 and 14.3, Fuji II LC and Photac Fil proved superior reliability in the flexural test, whereas GCP achieved a Weibull modulus of only 1.4 - 2.6. Low differences between the four GCP groups are indicated which are not significant.

#### *Vickers Hardness, indentation modulus and creep*

In the universal hardness test the values of the Vickers Hardness varied between 57.9 - 68.5 N/mm<sup>2</sup> (Fuji II LC and GCP) and 45.5 - 48.6 N/mm<sup>2</sup> (Photac Fil) (Table 3). Also, the highest indentation moduli were achieved by Fuji II LC and GCP (14.9 - 13.4 GPa), while Photac Fil reached the minimum value. The percentage of creep measured in the universal hardness test varied between 3.6 - 4.2% (GCP) and 5.0 - 5.6% (RMGICs). No significant differences between the four GCP groups were detected.

**Table 3 - Micro-mechanical properties.****VH:**

<b>Material</b>	<b>Top</b>	<b>Bottom</b>	<b>p</b>
Fuji II LC	63.4 <sup>b</sup> (6.9)	57.9 <sup>B</sup> (4.4)	0.05 (NS)
Photac Fil	48.6 <sup>a</sup> (4.4)	45.5 <sup>A</sup> (7.2)	0.27 (NS)
GCP 1	67.4 <sup>b</sup> (4.9)	64.7 <sup>BC</sup> (5.7)	0.27 (NS)
GCP 2	62.3 <sup>b</sup> (4.3)	67.9 <sup>C</sup> (6.8)	0.04
GCP 3	67.6 <sup>b</sup> (3.5)	63.3 <sup>BC</sup> (3.5)	0.01
GCP 4	65.7 <sup>b</sup> (5.3)	68.5 <sup>C</sup> (3.7)	0.19 (NS)

**E:**

<b>Material</b>	<b>Top</b>	<b>Bottom</b>	<b>p</b>
Fuji II LC	14.9 <sup>c</sup> (1.1)	14.3 <sup>A</sup> (0.6)	0.16 (NS)
Photac Fil	12.8 <sup>a</sup> (1.0)	13.2 <sup>A</sup> (1.7)	0.45 (NS)
GCP 1	14.3 <sup>bc</sup> (1.0)	13.8 <sup>A</sup> (0.8)	0.25 (NS)
GCP 2	13.4 <sup>ab</sup> (0.9)	14.5 <sup>A</sup> (0.8)	0.01
GCP 3	14.6 <sup>bc</sup> (0.4)	13.4 <sup>A</sup> (0.7)	0.00
GCP 4	14.2 <sup>bc</sup> (1.0)	14.4 <sup>A</sup> (0.8)	0.54 (NS)

**Cr:**

<b>Material</b>	<b>Top</b>	<b>Bottom</b>	<b>p</b>
Fuji II LC	5.1 <sup>d</sup> (0.4)	5.0 <sup>B</sup> (0.3)	0.76 (NS)
Photac Fil	5.6 <sup>e</sup> (0.3)	5.4 <sup>C</sup> (0.4)	0.36 (NS)
GCP 1	3.6 <sup>a</sup> (0.3)	3.9 <sup>A</sup> (0.4)	0.05 (NS)
GCP 2	4.2 <sup>c</sup> (0.2)	3.8 <sup>A</sup> (0.3)	0.00
GCP 3	3.8 <sup>ab</sup> (0.2)	4.2 <sup>A</sup> (0.3)	0.00
GCP 4	4.1 <sup>bc</sup> (0.1)	4.1 <sup>A</sup> (0.2)	0.78 (NS)

Vickers Hardness (VH, N/mm<sup>2</sup>), indentation modulus (E, GPa) and creep (Cr at 500 mN, %) of the top and bottom surface in mean values and standard deviations (in parentheses). Superscript letters indicate statistically homogeneous subgroups within a column (Tukey's HSD test,  $\alpha = 0.05$ ). A t-test analysed differences as function of the top and bottom (p, NS = non-significant).

*Influence of material and surface on Vickers Hardness, indentation modulus and creep*

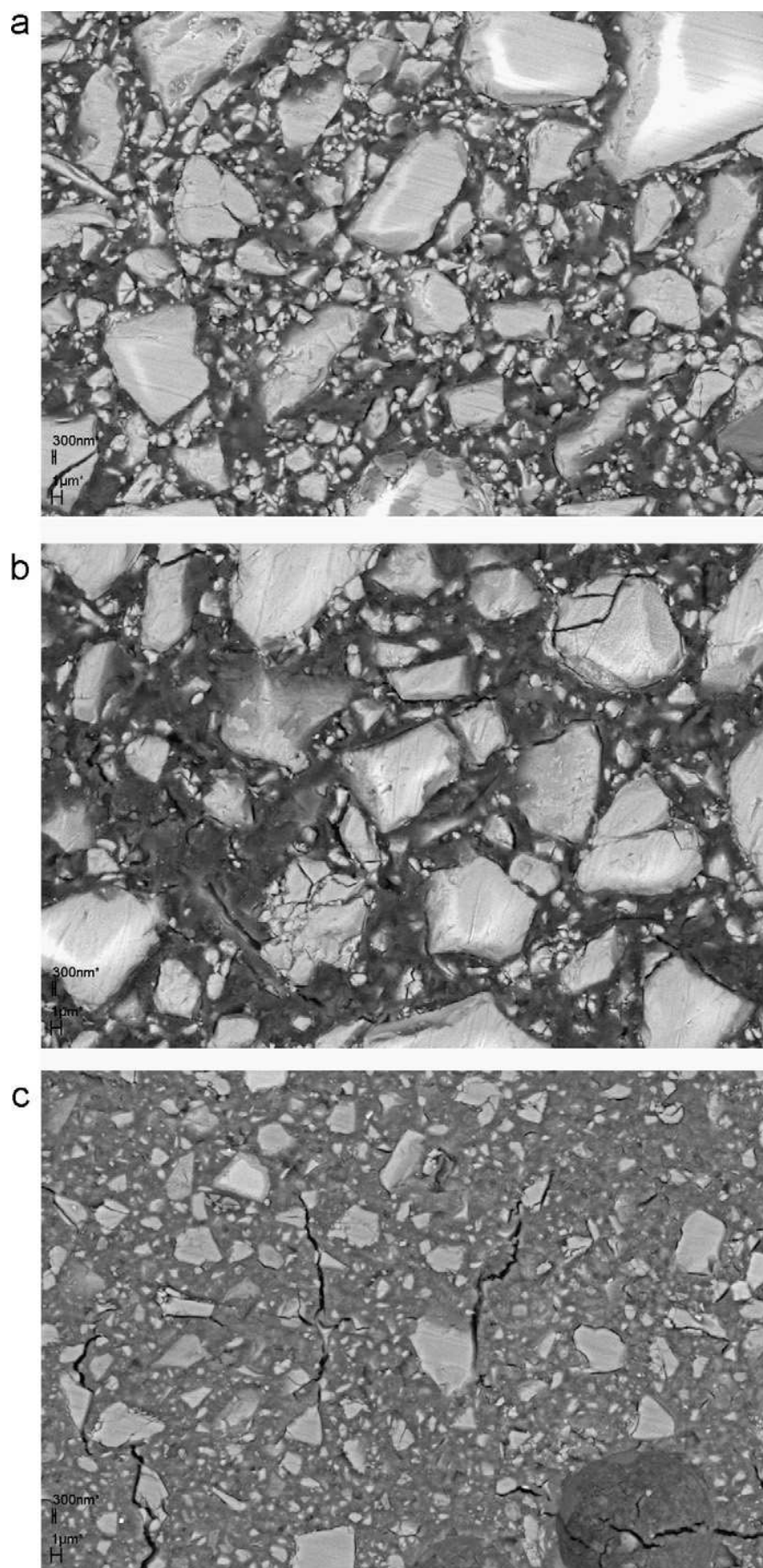
The multivariate analysis indicated that the material had a significant influence on the micro-mechanical properties, whereas the surface (top or bottom) showed no influence. The highest effect of the material was observed by creep (eta-squared = 0.85), followed by Vickers Hardness (0.66), while the effect of the material on the indentation modulus was lower (0.23). In the t-test no difference in micro-mechanical properties between the top and bottom surface of Fuji II LC, Photac Fil, GCP 1 and

GCP 4 was detected, whereas the top and bottom surface of GCP 2 and GCP 3 differed significantly ( $p = 0.00 - 0.04$ ) (Table 3).

#### *Light microscope and SEM analysis*

Comparing the samples in the light microscope of the universal hardness device, cracks and voids were ubiquitously observed within the matrix of all cements. The number of voids and cracks was generally greater for GCP than for RMGICs. In the SEM the RMGICs, Photac Fil and Fuji II LC showed a similar surface morphology: large glass particles were observed in the microstructures compared to GCP. The surface texture of Fuji II LC and GCP contained more fillers than Photac Fil.

**Figure 2** - SEM images of the cements (a) Fuji II LC, (b) Photac Fil, and (c) GCP.



## Discussion

In vitro studies allow the analysis of selected variables for a better understanding of materials' behaviour as well as the forecasting of its performance. Even when presenting some limitations, compared to clinical conditions, in vitro studies are necessary to provide important data of new dental materials.<sup>25</sup> GICs are clinically attractive dental materials and the requirement to strengthen these cements has led to an increasing research effort into reinforcement and strengthening concepts. The present study analysed the effect of gloss and heat on the mechanical behaviour of a glass carbomer cement. In addition, the mechanical properties were compared to well-known RMGICs. In all materials the top and bottom surfaces of the cements were examined.

Heat treatment and gloss application did not influence the mechanical behaviour of GCP after one week. Due to their moisture sensitivity, cements are frequently said to be technique sensitive. To maintain the water balance in cements, the surface of a newly placed restoration should be protected from water loss and also from water gain.<sup>26</sup> Therefore, on the one hand using GCP gloss helps to protect the material from desiccation and on the other hand it helps modelling and polishing fillings. Protecting cGICs (Riva Self Cure, SDI Limited, Victoria, Australia; Chemfil Rock, Dentsply, Konstanz, Germany; Fuji IX GP Fast, GC Europe N.V., Leuven, Belgium; Equia, GC Europe N.V., Leuven, Belgium) with a coating resulted in a significant higher flexural strength,<sup>27</sup> whereas gloss application showed no influence on the mechanical behaviour of GCP. The reason might be a difference between chemical compositions and thus, different moisture sensitivity of the cements. GCP gloss is monomer free and consists of modified polysiloxanes (Table 1), whereas coatings used to protect cGIC mostly consist of acrylic or methacrylic monomers which can be polymerised according to the manufacturer.

Also, heat treatment with an LED curing unit simulating clinical viable conditions showed no effect on the mechanical behaviour of the glass carbomer cement. The use of heat is supposed to accelerate the matrix-forming reaction of cements.<sup>17, 19</sup> While some studies have reported positive effects of heat on mechanical properties of cGICs,<sup>16, 17</sup> other studies indicated that different polymerisation units (e.g. heat) did not influence the strength of GCP (Elipar Freelight, 3M ESPE, Seefeld Germany, 1000 mW/cm<sup>2</sup>; Bluephase, Vivadent, Schaan, Liechtenstein, 1200 mW/cm<sup>2</sup> and Bluephase 16i, Vivadent,

Schaan, Liechtenstein, 1600 mW/cm<sup>2</sup>).<sup>19</sup> Using different polymerisation units did not show significant difference in the micro-hardness for the upper and lower surface of the specimens tested after 24 h storage in 100% humidity.<sup>18</sup> Heat treatment increased the micro-hardness of cGICs after 24 h,<sup>17</sup> whereas no effect of heat on the mechanical behaviour of GCP was measured. On the one hand, this fact can again be explained by a difference between chemical compositions. The GCP gloss is monomer free, whereas coatings used to protect cGIC mostly consist of monomers which can be polymerised and thus assure a better isolation and protection from exposure to moisture. On the other hand, prior to the universal hardness test the samples were ground with grinding silicon carbide paper and thus, a surface layer of approximately 100 µm was eliminated. This was done to allow a comparison with real clinical conditions, since in patients, after the cement is cured, the filling must also be polished.

One disadvantage of GCP is the high viscosity compared to the RMGICs. Filling the mould or teeth with GCP and producing exact samples and dense fillings is harder compared to the RMGICs which can flow easier under pressure. In this study the samples were stored in distilled water and not in saliva as saliva storage showed no influence on the mechanical properties of cGICs.<sup>27</sup> A visual inspection of the prepared GCP samples by using the transparent gloss revealed no surface cracks compared to the samples without gloss. The cracks were caused by dehydration as the surface of the cement was not protected by gloss. However, this aspect was not significant reflected in the measured mechanical properties.

GCP is self-curing and therefore chemically similar to cGICs. Nevertheless, in our study GCP was compared to RMGICs as the macro- and micro-mechanical properties of cGICs were already analysed in a similar study. A comparison between GCP and cGICs is given below. A high flexural and compressive strength is desired which enhances the longevity of a GIC by withstanding mastication forces.<sup>15</sup> The modulus of elasticity is an important parameter because it is a measure of the ability of a material to resist elastic deformation during loading.<sup>28</sup> As it is determined by bending forces between atoms, the modulus of elasticity is the most structure sensitive of the basic material properties. Therefore, it is a useful parameter to follow overtime changes within a material or to compare materials among each other.<sup>28</sup> Regarding the macroscopic mechanical properties, GCP was inferior to

the tested RMGICs after one week of storage. Tested after 24 h, the RMGICs analysed in our study (Fuji II LC Improved, Photac Fil) were shown to perform significantly better when compared to cGICs (Fuji IX, GC, Leuven, Belgium and Ionofil Molar, Cuxhaven, Germany).<sup>29</sup> Due to the snap resin crosslinking upon photo-polymerisation of RMGICs, previous studies also reported a two to three times higher compressive strength compared to cGICs at initial setting stage of the first 24 h.<sup>30</sup> Comparing GCP to cGICs (Riva Self Cure, Chemfil Rock, Fuji IX GP Fast and Equia) a higher flexural strength was observed for cGICs (14.3 - 39.4 MPa) measured at the same storing condition.<sup>27</sup> However other studies reported at earlier stage (24 h) a higher flexural strength for GCP than for cGIC (Fuji IX GP Fast),<sup>22</sup> a fact that might be attributed to the nano particles in the GCP structure and thus, an accelerating setting reaction due to an increased total filler surface. Analysing only the mean values and standard deviations for the strength of inhomogeneous materials does not offer sufficient information. For this reason the Weibull analysis for the flexural strength was added where the degree of dispersion  $m$  (Weibull parameter) shows the homogeneity of materials. High  $m$  parameters provide superior reliability. Thus, the measured RMGICs were proved to be more reliable compared to the GCP, irrespective of an additionally gloss or heat conditioning.

Conversely to the flexural test, the parameters analysed in the universal hardness test for GCP were superior to the RMGICs. In comparison to cGICs (Riva Self Cure, Chemfil Rock, Fuji IX GP Fast and Equia),<sup>27</sup> GCP offers poor mechanical properties. GCP showed a lower Vickers Hardness and indentation modulus than cGICs (VH: 66.8 - 125.9 N/mm<sup>2</sup>; E: 17.1 - 25.7 GPa) measured at the same storing conditions.<sup>27</sup> The relative indentation depth at a constant test load of 500 mN held for 5 seconds is a measure for the creep of a material and another important characteristic to evaluate the mechanical properties of a material. With a relative indentation depth of 3.6 - 4.2%, GCP offered more stability under load than RMGICs (5.0 - 5.6%).

Differences in mechanical behaviour exist between RMGICs and GCP but the mechanical properties did not differ between the upper and lower surface of Photac Fil, Fuji II LC and GCP groups 1 and 4. The small differences between top and bottom surface of GCP groups 2 and 3 might be a result of varying room temperature and moisture conditions during producing the samples.



The results of this study proved that relationships exist between the composition, microstructure and mechanical properties of the cements. The RMGICs reached a significantly higher flexural strength, whereas GCP generally achieved higher values of Vickers Hardness and lower values of creep. The larger glass particle sizes, less voids and cracks of the RMGICs resulted in higher values of flexural strength. Toughness of materials is related to crack size and crack size is related to microstructural features (e.g. filler size and porosity) and critical to the effective value of toughness (e.g. fracture resistance).<sup>31</sup> The smaller glass particle sizes of GCP were correlated with higher Vickers Hardness and lower creep. The nanoparticles increased the reactive surface of GCP and thus, led to a higher hardness.<sup>32</sup> Fuji II LC and GCP achieved a significant higher modulus of elasticity in flexural test and indentation modulus than Photac Fil. More glass filler particles in the surface texture in Fuji II LC and GCP resulted in higher values of modulus of elasticity in flexural test and indentation modulus. The chemical composition and different polymers may be another possible reason for the variations in mechanical properties of the cements tested. All three cements consist of different silicate glasses but the RMGICs Fuji II LC and Photac Fil also contain monomers which can be polymerised (Table 1) contributing thus to significantly higher flexural strength due to the dual-curing system.<sup>5</sup>

During the last few years concerns have been raised regarding the biocompatibility of the RMGICs. Filling and sealing material including RMGICs often contains the toxic (co)monomers hydroxyethylmethacrylate (HEMA), triethyleneglycoldimethacrylate (TEGDMA), urethanedimethacrylate (UDMA) and bisglycidylmethacrylate (BisGMA).<sup>33</sup> The resin (co)monomers may be released from restorative dental materials and can diffuse into the pulp, the gingiva, the saliva and the circulating blood.<sup>33</sup> Numerous cytotoxic responses to dental composite resins have been described.<sup>34</sup> It can lead to a variety of adverse biological effects in the patient, from persistent inflammation to sensitisation and potential allergic reactions.<sup>35</sup> There are potential problems of long-term exposure to HEMA in particular for dental personnel.<sup>35</sup> Besides contact dermatitis and other immunological responses, HEMA is volatile and its vapour can be readily inhaled, causing adverse reactions in the respiratory system.<sup>35</sup> One advantage of GCP and cGICs is that it is biocompatible and monomer free compared to RMGICs. Besides, RMGICs are considered to produce an exothermic setting reaction and thus, a greater temperature rise than cGICs.<sup>2</sup> However, this fact has not been shown to be a clinical

issue.<sup>2</sup> Clinically, RMGICs and cGICs are used in similar indications. Due to the rapid set, RMGICs are more attractive in patients with low compliance like children.<sup>8</sup> On the other hand, the higher fluoride release is one major argument for the use of cGICs in high caries risk patients.<sup>36</sup>

## Conclusions

Several attempts in improving the mechanical behaviour of cements were made. In this study, no effect of heat treatment and gloss application on the mechanical properties of GCP was measured. The mechanical properties were basically influenced by the type of cement and its microstructure. Macroscopically, the RMGICs performed significantly better than GCP. Conversely, in the universal hardness test GCP was superior to the RMGICs.

## References

1. Chen X, Du MQ, Fan MW, Mulder J, Huysmans MC, Frencken JE. Caries-preventive effect of sealants produced with altered glass-ionomer materials, after 2 years. *Dental Materials* 2012; **28**: 554-60.
2. Sidhu SK. Glass-ionomer cement restorative materials: a sticky subject? *Australian Dental Journal* 2011; **56**: 23-30.
3. Glasspoole EA, Erickson RL, Davidson CL. Effect of surface treatments on the bond strength of glass ionomers to enamel. *Dental Materials* 2002; **18**: 454-62.
4. Wiegand A, Buchalla W, Attin T. Review on fluoride-releasing restorative materials - fluoride release and uptake characteristics, antibacterial activity and influence on caries formation. *Dental Materials* 2007; **23**: 343-62.
5. Xie D, Brantley WA, Culbertson BM, Wang G. Mechanical properties and microstructures of glass-ionomer cements. *Dental Materials* 2000; **16**: 129-38.
6. Zanata RL, Fagundes TC, Freitas MC, Lauris JR, Navarro MF. Ten-year survival of ART restorations in permanent posterior teeth. *Clinical Oral Investigations* 2011; **15**: 265-71.
7. Mahoney E, Kilpatrick N, Johnston T. Restorative paediatric dentistry. In: Cameron AC, Widmer RP, editors. *Handbook of Pediatric Dentistry*. 3rd ed. Maryland Heights: Mosby; 2008. p.71-93.

8. Lohbauer U. Dental Glass Ionomer Cements as Permanent Filling Materials? —Properties, Limitations and Future Trends. *Materials* 2010; **3**: 76-96.
9. Hickel R, Manhart J, García-Godoy F. Clinical results and new developments of direct posterior restorations. *American Journal of Dentistry* 2000; **13**: 41-54.
10. Cho SY, Cheng AC. A Review of Glass Ionomer Restorations in the Primary Dentition. *Journal of the Canadian Dental Association* 1999; **65**: 491-5.
11. Frankenberger R, Garcia-Godoy F, Krämer N. Clinical Performance of Viscous Glass Ionomer Cement in Posterior Cavities over Two Years. *International Journal of Dentistry* 2009; DOI: 10.1155/2009/781462.
12. Moshaverinia A, Ansari S, Moshaverinia M, Roohpour N, Darr JA, Rehman I. Effects of incorporation of hydroxyapatite and fluoroapatite nanobioceramics into conventional glass ionomer cements (GIC). *Acta Biomaterialia* 2008; **4**: 432-40.
13. Mitra SB. Adhesion to dentin and physical properties of a light-cured glass-ionomer liner/base. *Journal of Dental Research* 1991; **70**: 72-4.
14. Uno S, Finger WJ, Fritz U. Long-term mechanical characteristics of resin modified glass ionomer restorative materials. *Dental Materials* 1996; **12**: 64-9.
15. Wang L, D'Alpino PHP, Lopes LG, Pereira JC. Mechanical properties of dental restorative materials: relative contribution of laboratory tests. *Journal of Applied Oral Science* 2003; **11**: 162-7.
16. Kleverlaan CJ, Van Duinen RNB, Feilzer AJ. Mechanical properties of glass ionomer cements affected by curing methods. *Dental Materials* 2004; **20**: 45-50.
17. Woolford MJ. Effect of radiant heat on the surface hardness of glass polyalkenoate (ionomer) cement. *Journal of Dentistry* 1994; **22**: 360-3.
18. Gorseta K, Glavina D, Negovetic Vranic D, Skrinjaric I. Microhardness of the new developed GlassCarbomer cement. Proceedings of the 88th General Session & Exhibition of the IADR; 2010 July 15-16; Barcelona, Spain.
19. Glavina D, Gorseta K, Negovetic Vranic D, Skrinjaric I. Enamel shear-bond strength of Glass Carbomer after heating with three polymerization unit. *International Journal of Paediatric Dentistry* 2009; **19**: 41.

20. Glavina D, Gorseta K, Negovetic Vranic D, Skrinjaric I. Retention of GlassCarbomer sealant after 6 months of clinical trial. Proceedings of the 88th General Session & Exhibition of the IADR; 2010 July 15-16; Barcelona, Spain.
21. Gorseta K, Glavina D, Skrinjaric I. Microleakage of newly developed nano ionomer and glass ionomer cement restoration. Proceedings of the 22nd Congress of the IADR; 2009 Sep 10-12; Munich, Germany.
22. Gorseta K, Negovetic Vranic D, Glavina D, Skrinjaric I. Effects of polymerisation unit on the flexural strength of Glass carbomer. *International Journal of Paediatric Dentistry* 2009; **19**: 75.
23. Koenraads H, Van Der Kroon G, Frencken JE. Compressive strength of two newly developed glass-ionomer materials for use with the Atraumatic Restorative Treatment (ART) approach in class II cavities. *Dental Materials* 2009; **25**: 551-6.
24. Schneider SJ. Engineered materials handbook. 4th ed. Materials Park, Ohio: ASM International; 1991. p.703-7.
25. Raggio DP, Branco EC, Calvo AFB, Bonifácio CC, Imparato JCP, Camargo LB. Knoop Hardness of Resin-modified Glass-ionomer Cements. *International Journal of Dentistry* 2009; **8**: 119-23.
26. Karaoğluoğlu S, Akgül N, Özdebak HN, Akgül HM. Effectiveness of surface protection for glass-ionomer, resin-modified glass-ionomer and polyacid-modified composite resins. *Dental Materials* 2009; **28**: 96-101.
27. Zoergiebel J, Ilie N. Evaluation of a conventional Glass Ionomer Cement with new zinc formulation: Effect of coating, aging and storage agents. *Clinical Oral Investigations* 2012; DOI: 10.1007.
28. Babu MR, Ravikiran V, Vinod V, Saraswathi D, Rao VN. Comparative Analysis for Selection of Resin Luting. Cements Based on Filler Content: An in vitro study. *The Journal of Contemporary Dental Practice* 2012; **13**: 481-6.
29. Ilie N, Hickel R. Mechanical behavior of glass ionomer cements as a function of loading condition and mixing procedure. *Dental Materials* 2007; **26**: 526-33.
30. Saito S, Tosaki S, Hirota K. Characteristics of glass ionomer cements. In: Davidson CL, Mjör IA, editors. *Advances in Glass-Ionomer Cements*. Berlin: Quintessence Publishing Co.; 1999. p.15-50.

31. Geirsson J, Thompson JY, Bayne SC. Porosity evaluation and pore size distribution of a novel directly placed ceramic restorative material. *Dental Materials* 2004; **20**: 987-95.
32. Prentice LH, Tyas MJ, Burrow MF. The effect of ytterbium fluoride and barium sulphate nanoparticles on the reactivity and strength of a glass-ionomer cement. *Dental Materials* 2006; **22**: 746-51.
33. Reichl FX, Esters M, Simon S, Seiss M, Kehe K, Kleinsasser N et al. Cell death effects of resin-based dental material compounds and mercurials in human gingival fibroblast. *Archives of Toxicology* 2006; **80**: 370-7.
34. Schwengberg S, Bohlen H, Kleinsasser N, Kehe K, Seiss M, Walther UI et al. In vitro embryotoxicity assessment with dental restorative materials. *Journal of Dentistry* 2005; **33**: 49-55.
35. Nicholson JW, Czarnecka B. The biocompatibility of resin-modified glass-ionomer cements for dentistry. *Dental Materials* 2008; **24**: 1702-8.
36. Al-Naimi OT, Itota T, Hobson RS, McCabe JF. Fluoride release for restorative materials and its effect on biofilm formation in natural saliva. *Journal of Material Science: Materials in Medicine* 2008; **19**: 1243-8.

### 3. Literaturverzeichnis

- [1] Sidhu SK. Glass-ionomer cement restorative materials: a sticky subject? *Austr Dent J*, 2011; 56:23-30.
- [2] Glasspoole EA, Erickson RL, Davidson CL. Effect of surface treatments on the bond strength of glass ionomers to enamel. *Dent Mater*, 2002; 18:454-462.
- [3] Wiegand A, Buchalla W, Attin T. Review on fluoride-releasing restorative materials - fluoride release and uptake characteristics, antibacterial activity and influence on caries formation. *Dent Mater*, 2007; 23:343-362.
- [4] Cho SY, Cheng AC. A Review of Glass Ionomer Restorations in the Primary Dentition. *J Can Dent*, 1999; 65:491-495.
- [5] Frankenberger R, Garcia-Godoy F, Krämer N. Clinical Performance of Viscous Glass Ionomer Cement in Posterior Cavities over Two Years. *Int J Dent*, 2009; DOI: 10.1155/2009/781462.
- [6] Moshaverinia A, Ansari S, Moshaverinia M, Roohpour N, Darr JA, Rehman I. Effects of incorporation of hydroxyapatite and fluoroapatite nanobioceramics into conventional glass ionomer cements (GIC). *Acta Biomater*, 2008; 4:432-440.
- [7] Kleverlaan CJ, Van Duinen RNB, Feilzer AJ. Mechanical properties of glass ionomer cements affected by curing methods. *Dent Mater*, 2004; 20:45-50.
- [8] Algea TJ, Kleverlaan CJ, Prahl-Andersena B, Feilzer AJ. The influence of environmental conditions on the material properties of setting glass-ionomer cements. *Dent Mater*, 2006; 22:852-856.
- [9] Talal A, Tanner KE, Billington R, Pearson GJ. Effect of ultrasound on the setting characteristics of glass ionomer cements studied by Fourier Transform Infrared Spectroscopy. *J Mater Sci Mater Med*, 2009; 20:405-411.
- [10] Woolford MJ. Effect of radiant heat on the surface hardness of glass polyalkenoate (ionomer) cement. *J Dent*, 1994; 22:360-363.
- [11] Chen X, Du MQ, Fan MW, Mulder J, Huysmans MC, Frencken JE. Caries-preventive effect of sealants produced with altered glass-ionomer materials, after 2 years. *Dent Mater*, 2012; 28:554-560.
- [12] Glavina D, Gorseta K, Negovetic Vranic D, Skrinjaric I. Enamel shear-bond strength of Glass Carbomer after heating with three polymerization unit. *Int J Paediatr Dent*, 2009; 19:41.

- [13] Glavina D, Gorseta K, Negovetic Vranic D, Skrinjaric I. Retention of GlassCarbomer sealant after 6 months of clinical trial. Proceedings of the 88th General Session & Exhibition of the IADR; 2010 July 15-16; Barcelona, Spain.
- [14] Gorseta K, Glavina D, Skrinjaric I. Microleakage of newly developed nano ionomer and glass ionomer cement restoration. Proceedings of the 22nd Congress of the IADR; 2009 Sep 10-12; Munich, Germany.
- [15] Gorseta K, Negovetic Vranic D, Glavina D, Skrinjaric I. Effects of polymerisation unit on the flexural strength of Glass carbomer. *Int J Paediatr Dent*, 2009; 19:75.
- [16] O'Brien T, Shoja-Assadi F, Lea SC, Burke FJT, Palin WM. Extrinsic energy sources affect hardness through depth during set of a glass ionomer cement. *J Dent*, 2010; 38:490-495.
- [17] Yap AUJ, Cheang PHN, Chay PL. Mechanical properties of two restorative reinforced glass-ionomer cements. *J Oral Rehabil*, 2002; 29:682-688.
- [18] Nicholson JW. Chemistry of glass-ionomer cements: a review. *Biomaterials*, 1998; 19:485-494.
- [19] Karaoğluoğlu S, Akgül N, Özdebak HN, Akgül HM. Effectiveness of surface protection for glass-ionomer, resin-modified glass-ionomer and polyacid-modified composite resins. *Dent Mater*, 2009; 28:96-101.
- [20] Zoergiebel J, Ilie N. Evaluation of a conventional Glass Ionomer Cement with new zinc formulation: Effect of coating, aging and storage agents. *Clin Oral Invest*, 2013; 17:619-626.
- [21] Ilie N, Hickel R. Mechanical behavior of glass ionomer cements as a function of loading condition and mixing procedure. *Dent Mater*, 2007; 26:526-533.
- [22] Tanner DA, Rushe N, Towler MR. Ultrasonically set glass polyalkenoate cements for orthodontic applications. *J Mater Sci Mater Med*, 2006; 17:313-318.
- [23] Prentice LH, Tyas MJ, Burrow MF. The effect of ytterbium fluoride and barium sulphate nanoparticles on the reactivity and strength of a glass-ionomer cement. *Dent Mater*, 2006; 22:746-751.
- [24] Xie D, Brantley WA, Culbertson BM, Wang G. Mechanical properties and microstructures of glass-ionomer cements. *Dent Mater*, 2000; 16:129-138.